



Faculty of Resource Science and Technology

Carbon Dots ZIF-8 Membrane for Lead(II) Removal

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Carbon Dots ZIF-8 Membrane for Lead(II) Removal

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DECLARATION

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



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ABSTRACT

Heavy metal pollution has become a significant problem in past years, owing to the fast growth of polluting industries. The most hazardous heavy metals, such as lead(II), might have catastrophic consequences for human health and this problem should be overcome. Therefore, a reasonable approach to tackle this issue is by introducing a membrane material derived from the combination of ZIF-8 and carbon dots material to remove the lead(II) from the aqueous solution. The aim of this research study is to fabricate carbon dots-ZIF-8 (CDs@ZIF-8) membrane and to evaluate the performance of modified ZIF-8 membrane on the removal of heavy metal. This study was conducted through three phases in brief. The study started with the preparation of CDs@ZIF-8 membrane which involved the preparation from sago *hampas*, modification of alumina hollow fibre membrane using APTES and in-situ solvothermal preparation. The second phase involved various kinds of characterization analysis; FTIR, SEM, EDX, XRD and PSA. Subsequently, the removal of lead(II) by CDs@ZIF-8 membrane performance had been evaluated through the batch adsorption study and cross-flow filtration system. The 160°C CDs@ZIF-8 membrane exhibits better adsorption performance than the 200°C CDs@ZIF-8 membrane with a maximum lead(II) absorption potential of 95.16 mg/g and remove up to 74.73% of the lead(II) ions with the flux of 38.55 Lm⁻²h⁻¹. The Freundlich isotherm and pseudo-second-order model best matched the lead(II) adsorption process onto the CDs@ZIF-8 membrane.

Keywords: Carbon Dots, ZIF-8, Membrane, Lead(II), Sago *Hampas*

Dots Karbon ZIF-8 Membran untuk Penyingkiran Logam Berat

ABSTRAK

Pencemaran logam berat telah menjadi masalah utama sejak beberapa tahun kebelakangan ini disebabkan oleh pertumbuhan pesat industri pencemar. Antara logam berat yang paling berbahaya ialah plumbum(II), yang boleh memberi kesan buruk terhadap kesihatan manusia dan perlu ditangani segera. Justeru itu, pendekatan yang sesuai untuk menangani isu ini adalah dengan memperkenalkan bahan membran yang terhasil daripada gabungan ZIF-8 dan karbon dots bagi menyingkirkan plumbum(II) daripada larutan akueus. Tujuan kajian ini adalah untuk menghasilkan membran CDs@ZIF-8 dan menilai prestasi membran ZIF-8 terubah suai dalam penyingkiran logam berat. Kajian ini dijalankan dalam tiga fasa utama. Fasa pertama melibatkan penyediaan membran CDs@ZIF-8 yang merangkumi pengekstrakan karbon totot daripada hampas sagu, pengubahsuaian membran serabut berongga alumina menggunakan APTES, serta proses penyediaan secara solvoterma in-situ. Fasa kedua merangkumi pelbagai analisis pencirian seperti FTIR, SEM, EDX, XRD dan PSA. Seterusnya, prestasi penyingkiran plumbum(II) oleh membran CDs@ZIF-8 telah dinilai melalui kajian penjerapan kelompok dan sistem penapisan aliran silang. Membran CDs@ZIF-8 pada suhu 160 °C menunjukkan prestasi penjerapan yang lebih baik berbanding membran pada suhu 200 °C, dengan kapasiti penjerapan maksimum plumbum(II) sebanyak 95.16 mg/g dan kadar penyingkiran mencapai 74.73% pada fluks 38.55 Lm⁻²j⁻¹. Model isoterma Freundlich dan kinetic model tertib pseudo-kedua menunjukkan kesesuaian terbaik bagi proses penjerapan plumbum(II) ke atas membran CDs@ZIF-8.

Kata kunci: Karbon dots, ZIF-8, Membran, Plumbum(II), Sago Hampas

TABLE OF CONTENTS

	Page
DECLARATION	i
ACKNOWLEDGEMENT	ii
ABSTRACT	iv
<i>ABSTRAK</i>	v
TABLE OF CONTENTS	vi
LIST OF TABLES	x
LIST OF FIGURES	xi
LIST OF ABBREVIATIONS	xiii
CHAPTER 1: INTRODUCTION	1
1.1 Study Background	1
1.2 Problem Statement	5
1.3 Objectives	7
1.4 Scope of study	7
CHAPTER 2: LITERATURE REVIEW	10
2.1 Industrial heavy metal pollution	10
2.1.1 Lead (Pb)	11
2.2 Lead (Pb) removal technologies	13

2.2.1	Electrochemical and electrolysis	14
2.2.2	Adsorption	15
2.2.3	Membrane separation technology	19
2.3	Type of membrane separation technology	22
2.3.1	Hollow fibre (HF) configuration	23
2.4	Ceramic membrane	26
2.5	Ceramic membrane preparation method	28
2.5.1	Sol gel method	28
2.5.2	Slip casting method	30
2.5.3	Phase inversion and co- sintering method	32
2.6	Adsorptive membrane	34
2.6.1	Adsorptive membrane for lead(II) removal	38
2.7	Metal organic framework (MOF)	40
2.7.1	Zeolitic imidazolate framework-8 (ZIF-8)	42
2.7.2	Limitation of ZIF-8	45
2.8	Nanomaterials	47
2.8.1	Carbon dots (CDs)	47
2.8.2	Carbon dots (CDs) synthesis	48
2.8.3	Biomass waste: sago <i>hampas</i>	51
2.9	Cross-flow filtration system	55

CHAPTER 3: METHODOLOGY	59
3.1 Materials	59
3.2 Preparation of carbon dots-ZIF-8 membrane	59
3.2.1 Preparation of carbon dots from sago <i>hampas</i>	59
3.2.2 Modification of alumina hollow fibre membrane using 3-(aminopropyl)triethoxysilane (APTES)	60
3.2.3 In-situ solvothermal preparation of carbon dots-ZIF-8 membrane	60
3.3 Membrane characterization	62
3.3.1 Scanning electron microscopy scanning (SEM) / Electron dispersive X-ray (EDX) spectroscopy	62
3.3.2 Ultraviolet-visible (UV-vis) analysis	63
3.3.3 Fourier transform infrared spectroscopy (FTIR) analysis	63
3.3.4 X-ray diffraction (XRD) analysis	63
3.4 Performance study on the removal of lead(II) by carbon-dots-ZIF-8 membrane	63
3.4.1 Batch adsorption study	63
3.5 Filtration study	65
CHAPTER 4: RESULTS AND DISCUSSION	67
4.1 Characterization of carbon quantum dots	67
4.1.1 UV-Visible Spectroscopy	67
4.1.2 Fourier transformed infrared (FTIR)	69

4.1.3	Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX)	71
4.1.4	X-ray diffraction analysis (XRD)	72
4.2	Characterization of Carbon Dots ZIF-8 Membrane (CDs@ZIF-8)	74
4.2.1	Fourier transformed infrared (FTIR)	74
4.2.2	Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX)	76
4.3	Performance study for lead(II) removal by ZIF-8/CDs membrane	80
4.3.1	Batch adsorption study on lead(II) removal	80
4.3.2	Adsorption isotherm	88
4.3.3	Kinetic study	89
4.3.4	Filtration study	92
CHAPTER 5: CONCLUSION AND RECOMMENDATIONS		96
5.1	Conclusion	96
5.2	Recommendations	97
REFERENCES		98

LIST OF TABLES

		Page
Table 1.1	Variety of industrial wastes and metals detected	2
Table 2.1	Some of the fundamental characteristics of membrane components	23
Table 2.2	Heavy metal removal with AMs has been the subject of several articles	36
Table 2.3	Nano-adsorbent properties in removing lead(II).	39
Table 2.4	The Stability of MOFs in Aqueous Solutions or Humid Environments	42
Table 2.5	The comparison of ZIF-8 composites and their synthesis method	46
Table 2.6	The carbon dots synthesis from biomass source and their applications	51
Table 3.1	Adsorption isotherms and kinetics models	64
Table 4.1	The solute flux and lead(II) rejection of CDs@ZIF-8 alumina membrane.	90

LIST OF FIGURES

	Page
Figure 2.1 Heavy metal removal mechanism by adsorbent	17
Figure 2.2 Ceramic hollow–fibre Membrane	25
Figure 2.3 (a)The inside-outside HF (bore-side feed) and (b) the outside-inside HF (shell-side feed)	26
Figure 2.4 A cross-sectional diagram of a ceramic membrane.	27
Figure 2.5 A sol-gel produced zirconium carbide–silicon carbide composite heated at 1500 °C for 1 hour at low and high SEM images magnification	30
Figure 2.6 Capillary suction and gravity force draw the solvent into mold's pores and a slip particles layer simultaneously formation on mold surfaces	31
Figure 2.7 The solidified layer also known as a cast, develops on mold's wall is shown in diagram	32
Figure 2.8 SEM image of the surface of the metakaolin-based flat sheet ceramic membrane. (a1, a2) sintered at 1,200 °C, (b1, b2) sintered at 1,300 °C, (c1, c2) sintered at 1,400 °C, and (d1, d2) sintered at 1,500 °C for 4 h. (a–d) Unmodified membrane, (a1–d1) modified membrane	33
Figure 2.9 ZIF-8 topology and crystal structure	45
Figure 2.10 The modification of ZIF-8 with functional materials species	46
Figure 2.11 Malaysian sago starch export data from 2008 to 2017	53
Figure 2.12 The extraction of sago starch is depicted in this flow diagram	56
Figure 2.13 a) Cross-flow and b) dead-end membrane filtration diagrams	57
Figure 2.14 CFF system operation route	58
Figure 3.1 The preparation of CDs through the hydrothermal method.	62
Figure 3.2 (a) In-situ solvothermal preparation of carbon dots-ZIF-8 membrane (b) the illustration of CDs@ZIF-8 membrane modification.	64
Figure 3.3 The schematic diagram of cross-flow filtration system.	69
Figure 4.1 The carbon dots 200°C (a) under the daylight and (b) under the shortwave uv lamp which compared with the distilled water sample,	

	carbon dots (left) and distilled water (right), (c) The carbon dots 200°C (left) and 160°C (right) under longwave uv lamp (d) Absorption curves (Abs) carbon dots 160°C (red spectra), 200°C (black spectra).	71
Figure 4.2	FTIR images of (a) carbon dots 160°C(red), 200°C(black) and sago <i>hampas</i> , (green) spectra CDs@ZIF membrane (red).	73
Figure 4.3	The SEM images of synthesized carbon dots (CDs); (a) 200°C and(b)160°C.	74
Figure 4.4	The XRD graph of 200 °C and 160 °C CDs (a).	74
Figure 4.5	FTIR images of 200°C and 160°C CDs@ZIF-8 membrane spectra.	77
Figure 4.6	The SEM images of surface, cross-sectional, EDX-mapping of unmodified alumina membrane (a,b,c), 200°C CDs@ZIF-8 membrane (d,e,f) and 160°C CDs@ZIF-8 membrane (g,h,i).	80
Figure 4.7	Effect of contact time on the lead(II) removal using carbon dots 200°C (black) and 160°C (red) modified membrane.	83
Figure 4.8	Effect of pH on the lead(II) removal by CD@ZIF-8 membrane	86
Figure 4.9	Adsorption capacity of carbon dots modified membrane membranes at different initial concentrations	87
Figure 4.10	Langmuir model (left) and Freundlich model (right)	91
Figure 4.11	First order (left) Second order (right)	91
Figure 4.12	The solute flux and lead(II) rejection of CDs@ZIF-8 alumina membrane	95

LIST OF ABBREVIATIONS

Ag	Silver
AgNCs	Silver Nanoclusters
Al	Aluminium
Al ₂ O ₃	Aluminium Oxide
AMs	Adsorptive Membranes
APTES	(3-Aminopropyl)triethoxysilane
As	Arsenic
ATR-FTIR	Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy
BC	Bacterial Cellulose
BDC	1, 4-Benze-Dicarboxylate
BET	Brunauer-Emmett-Teller
BOD	Biochemical Oxygen Demand
BTC	Benzene-1, 3, 5-tricarboxylic Acid
CA	Cellulose Acetate
Ca	Calcium
CDs	Carbon Dots
Cd	Cadmium

CNTs	Carbon Nanotubes
COD	Chemical Oxygen Demand
COOH	Carboxylic Acid
Cr	Chromium
CTS	Chitosan
Cu	Copper
DAS	Department of Agriculture Sarawak
DMF	N, N-dimethylformamide
DTPA	Pentetic acid
EC	Electrocoagulation
EDTA	Ethylenediaminetetraacetic acid
EF	Electroflotation
EFB	Empty Fruit Brunch
ENMs	Electrospinning Nanofiber Membranes
EO	Electrooxidation
EPA	Environmental Protection Agency
EDX	Energy Dispersive X-Ray
FESEM	Field-Emission Scanning Electron Microscopy
FO	Forward Osmosis

HF	Hollow Fiber
Hg	Mercury
HKUST	Hong Kong University of Science and Technology
HPI	Heavy Metal Pollution Index
HP-UiO-66	Hierarchically porous Universitetet i Oslo-66
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
MF	Microfiltration
MgO	Magnesium Oxide
MIL-88B	Material Institut Lavoisier
mIm	2-Methylimidazole
MnO ₂	Magnesium Dioxide
MOFs	Metal Organic Frameworks
MoS ₂	Molybdenum Disulfide
MWCO	Molecular Weight Cut Off
NCDs	Nitrogen-doped Carbon Dots
NEMs	Nano-enhanced Membranes
NF	Nanofiltration
NH ₂	Amino Radical (Azanide)
Ni	Nickel

NMP	N-methyl-2-pyrrolidone
NTA	Nitrilotriacetic acid
PAN	Ploy(acrylonitrile)
PANI	Polyaniline
PANIB	Bentonite
Pb	Lead
PCL	Polycaprolactone
PCMs	Polyceramic Membranes
PEI	Poly(ethyleneimine)
PESf	Polyethersulfone
pH	Potential of Hydrogen
PMs	Polymeric Membranes
POMs	Polyoxometalates
Ppb	Parts Per Billion
PSA	Particle Size Analyer
PSf	Polysulfone
PTFE	Poly(tetrafluoroethylene)
PVA	Poly(Vinyl Alcohol)
PVC	Polyvinyl Chloride

PXRD	Powder X-ray Diffraction
rGO	Reduced Graphene Oxide
RO	Reverse Osmosis
SEM	Scanning Electron Microscope
Si	Silicon
SiO ₂	Silicon Dioxide
SO ₃ H	Sulfonic Acid
TC	Thiol-Functionalized Cellulose
TFN	Thin Film Nanocomposite
Ti	Titanium
TiO ₂	Titanium Dioxide
TMP	Transmembrane Pressure
TPPP	Tetra(4-Phosphonophenyl)porphyrin
UF	Ultrafiltration
UiO-66	Universitetet i Oslo-66
USEPA	United States Environmental Protection Agency
WHO	World Human Organization
XRD	X-ray Diffraction
YSZ	Yttria-Stabilized Zirconia

Zeo	Zeolite
ZIF-8	Zeolite Imidazolate Framework-8
Zr	Zirconium
ZrO ₂	Zirconium Dioxide
Zn	Zinc
Zn(NO ₃) ₂ ·6H ₂ O	Zinc Nitrate Hexahydrate

CHAPTER 1

INTRODUCTION

1.1 Study Background

With the improvement of social economy and the heightening of human exercises, the enormous measure of wastewater released by industrial sectors will damage the aquatic climate, in this manner truly influencing the use of water supplies and the construction of water environments (Aftab et al., 2019). The rapid development of polluting industries such as pharmaceutical drugs, fabric, agrochemicals, tanneries, and heavy industries, as well as rising life norms, global population, and urban development, have contributed to the production of harmful and unmanageable wastewater incorporating hazardous pollutants around the world in previous years (Malik et al., 2020). In the past recent year, heavy metal pollution has become a serious issue among people from all walks of life as its fixations are expanding at a disturbing rate owing to the spontaneous industrialization and development expand (Maeaba et al., 2020). In India, roughly 44 million m³ of industrial effluent is created every day, of which nearly 6.2 billion litres are dumped into natural aquatic bodies untreated (Dutta et al., 2021). This statistic is presented to illustrate the scale of industrial wastewater discharge in large, rapidly industrializing nations. Meanwhile, in Malaysia, 189 rivers were reported to be polluted in 2017, with 72 classified as slightly polluted and 17 as polluted, largely due to effluent discharge from factories, sewage treatment plants, and agricultural runoff (Muda et al., 2022). River pollution remains a critical environmental issue, with regulatory gaps and enforcement weaknesses contributing to water quality deterioration in major rivers such as the Klang and Sungai Melaka (Mokhtar et al., 2023). Different kinds of

heavy metals were detected in wastewater due to industries activities that being carried nowadays, as illustrated Table 1.1

Table 1.1: Variety of industrial wastes and metals detected (Dutta *et al.*, 2021)

Industries	Heavy Metal Detected
Chemical	Cd, Pb, Cu, Cr, Zn, Hg, As, Fe, Ni
Distillery	Cd, Cu Cr, Pb, Zn
Sugar	As, Cd, Cu, Cr, Pb, Hg
Food and Dairy	Cd, Fe, Pb, Zn, Cu
Pulp and paper	Cd, Cu, Pb, Zn, Cr
Tannery	Zn, As, Pb, Cr, Cu, Cd
Plastic and resins	Cd, Cr, Pb, Hg, Sb, Sn
Detergents and soaps	Zn, Pb, Mn, Grease and oil, Cl, Na, K, Ca,

The introduction of heavy metal effluent into aquatic bodies is a major source of pollution which not only poses a major threat to aquatic creatures and public health, but it also results in considerable economic consequences due to the inability to recycle heavy metal wastewater (Sun et al., 2019). Because of their negative impacts on aquatic life, humans, and animals, the disposal of such highly polluted effluents can cause a major ecological imbalance (Sheth et al., 2021). High levels of pollution in the human body can cause cancer, skin infections that cause staining and itching, weakened vision, respiratory issues, and other disorders (Sun et al., 2020).

It was formerly feasible to remove different heavy metals from wastewaters via membrane and sorption filtration, ion-exchange resins, and electrochemical and chemical precipitation, however, these types of methods have many restrictions for example, reduced selectivity, higher operating expenses, and partial metal ion removal of less than 50 ppm, as well as the production of metal-containing sludge (Das et al., 2021). The adsorption approach

stands out among the techniques because of its versatility in operation and design procedures, and it appears to have a substantial impact on toxicity, biological availability, and heavy metal transport in wastewater (Chai et al., 2021). Nonetheless, adsorption has several disadvantages, the difficulty to achieve satisfactory commercial status owing to a lack of suitable high- adsorption-capacity adsorbents and commercial- scale columns (Sadegh and Ali, 2021). Although adsorption can remove the majority of water contaminants, it has certain drawbacks, such as a shortage of suitable adsorbents with high adsorption capacity and a limited commercial usage of these adsorbents (Nqombolo et al., 2018). To such a degree, more efficient approaches such as membrane technology have become necessary.

The environment and human health are both harmed by the untreated sewage from these heavy metals-discharged industries where heavy metals are particularly non-biodegradable (in contrast with organic pollutants) and portray a serious health concern when they reach the human food chain (Gnanasekaran et al., 2019). Multiple organ impairment, birth abnormalities, learning disabilities, and carcinogenicity are all caused by these metals (Li et al., 2021). Electroplating, mining, battery producing, metallurgy, tannery, and metal plating are just a few of the sectors that emit effluents containing generally high amounts of heavy metals like copper, cadmium, nickel, mercury, and lead (Li et al., 2021). Between the mentioned heavy metals, lead(II) contamination is receiving a lot of attention these days because of its severe neurotoxicity and hematotoxicity and the lead(II) ion is easily absorbed and aggregates over time in the human body, causing neurasthenia, anaemia, anorexia, stomach pain, diarrhoea, and kidney impairment (Tao et al., 2020). Therefore, it is critical to develop and construct efficient materials or technology to remove lead(II) from wastewaters before they are discharged.

As a result, materials having a high absorption capacity for heavy metal removal are critically needed in order to prevent heavy metals contamination. Metal-organic frameworks (MOFs) have been produced in recent years using molecules containing variety of inorganic metal ions centres and organic ligands while they also may be used to produce a wide range of specific applications (Tang et al., 2019). Pursuant to Li et al. (2017), MOFs have attracted a lot of interest for a variety of industrial purposes, including membrane separation, due to their inherent porosity properties, chemical flexibility, abundance of functions and characterized with fixed and highly tunable pore configuration, as well as a wide range of secondary building units linked by multitopic organic ligands and linker topology, and connectivity, making them preferable to customary porous materials like zeolites and carbon-based materials. The long-term removal of heavy metals from aqueous solutions is growing in popularity. Several approaches have been used to certify that heavy-metal concentrations in wastewater are reduced to fulfil Environmental Protection Agency (EPA) regulations (Li et al., 2021). Many scientists have recently been interested in MOFs, notably ZIF-8 (Zeolitic imidazolate framework-8), due to its distinctive attributes, such as large surface area, high adsorption ability, thermochemical stability, hydrophobicity, and practicable room-temperature synthesis (Abbasi et al., 2019).

However, under ambient settings, ZIF-8 crystallites are not stable in water where the zinc and imidazolate ions formed are dissolved in the water (Zhang et al., 2019). In fact, both ZIF-8 crystals and ZIF-8 membranes deteriorate in water due to disintegration at ambient temperature. The degradation rate increases when the ZIF-8 mass-to-water ratio or the concentration of 2-methylimidazolate in the aqueous solution decreases, indicating that ZIF-8 membranes are significantly less stable than ZIF-8 crystals (Zhang et al., 2017). Therefore, the modification of ZIF-8 by encapsulation with the carbon dots in the pores of ZIF-8 is

predicted to improve hydrostability. As reported by Gao et al. (2020b), the encapsulated enzymes in ZIF-8 are more stable under severe circumstances than their free equivalents, for as at high temperatures, in the existence of organic solvent, or at extreme pH levels. Although only limited research has been conducted on the hydrostability of carbon dots–ZIF-8 composites, their stability in water is considered crucial, as it directly affects their performance in lead(II) removal from wastewater.

Study by Zhuang et al., (2019) shows that by encapsulation of silver nanoclusters (AgNCs) in ZIF-8 have a high capacity to remove Pb^{2+} from water. This suggests that functionalizing ZIF-8 with nanoparticles can improve its adsorption performance. In this study, carbon dots were selected as the modifying agent due to their abundant surface functional groups, good dispersibility, and known ability to enhance metal ion binding. Therefore, the performance of carbon dots–ZIF-8 membranes for heavy metal removal was evaluated. Additionally, their structural stability in water was investigated to assess the lead(II) adsorption behavior and related physicochemical properties.

1.2 Problem Statement

Metal-organic frameworks (MOFs), a type of metallic coordination polymer formed by connecting metal atoms with organic linkers, have gained significant attention due to their customizable chemical properties and versatile structures. Recent progress in MOFs-based wastewater treatment, particularly in eliminating trace heavy metal ions like Hg^{2+} , Pb^{2+} , and Cd^{2+} from water, has been notable (Li et al., 2021). Among MOFs, Zeolitic imidazolate frameworks-8 (ZIF-8), is well-known for its high chemical and water stability, large surface area, and numerous active surface sites (Abbasi et al., 2019). Nevertheless, akin to other adsorbents, ZIF-8 particles are commonly synthesized as dispersed powders, posing

challenges in adsorption/regeneration processes and potential safety risks due to possible leakage into water supplies. To meet practical application requirements, it is essential to support or shape the powder materials appropriately (Zhang et al., 2019). To date, as the exploration of novel MOFs and the investigation of their properties and applications continue to progress rapidly, there has been a growing focus on the study of MOF-based composite materials. This involves combining MOFs with other components. For instance, integrating the porosity of MOFs with fluorescent materials like quantum dots (QDs), fluorescent dyes, or carbon dots (CDs) enables the creation of composites with enhanced properties suitable for applications in sensing, photocatalysis, and energy (Wang et al., 2019). These applications are considered highly commendable. In contrast to single ZIF-8, the utilization of ZIF-8 composites offers several advantages: it (i) reduces the aggregation of the adsorbent, (ii) facilitates the separation of the adsorbent from water, and (iii) enhances the active sites and stability of the adsorbent. This results in superior adsorption capabilities and improved recyclability compared to the individual constituents when treating water pollutants. This research aims to establish the theoretical groundwork for employing ZIF-8 composites in wastewater treatment. It introduces innovative concepts by encapsulating carbon dots (CDs) in ZIF-8 pores to improve the properties of ZIF-8 in terms of its adsorption capability.

In many instances, a robust interaction exists between adsorbents and heavy metals. Nevertheless, the technical complexity or high cost associated with the desorption process for regenerating and reusing the adsorbent is often considered a significant drawback of these materials. Additionally, the conventional disposal method for waste adsorbents containing heavy metal ions involves sending them to landfills. Inadequate handling of these waste materials may result in the release of heavy metals, contributing to secondary environmental

pollution. Consequently, researchers frequently use for composite structures involving ZIF-8 and other materials as adsorbents for water pollutant removal. However, there is a notable scarcity of studies examining the adsorption mechanism of ZIF-8 itself in relation to heavy metals. To tackle these challenges, the current research suggests combining the benefits of adsorption with membrane technology to create an adsorptive membrane. Therefore, in this study, incorporating alumina hollow fiber membrane as a supporting medium eased the fixation of CDs@ZIF-8 composite, allowing for favorable separation from the reaction mixtures. This method is designed to produce a novel MOF- composite membrane, CDs@ZIF-8 alumina membrane to effectively remove lead(II) from aqueous solutions, simulating wastewater conditions.

1.3 Objectives

The main objectives of this study were:

- i. To study the effects of synthesis temperature on the morphology of carbon dots derived from sago *hampas*
- ii. To determine the effect of different carbon dots on the physicochemical properties of CD@ZIF-8 membrane
- iii. To evaluate the performance of carbon dots ZIF-8 membrane on the removal of heavy metal specifically lead(II).

1.4 Scope of study

In order to achieve the objectives of the research, the scopes are focused as listed below:

- 1) To determine the effect of synthesis temperature on the morphology of carbon dots derived from sago *hampas*:
 - i) Synthesis of carbon dots using a hydrothermal process using sago waste as the carbon source and ammonia as the nitrogen supply. The carbon dots were prepared for 8 hours heating at 160°C, and 200°C, respectively.
 - ii) After then, the reactor was naturally cool to normal temperature. The crude product then filtered with 0.45 µm filter membranes to remove large particles, and then centrifuged to separate the supernatant and residues.
 - iii) Characterization of the carbon dots solution through UV-vis spectrophotometer (Cary 60 UV-Vis, Agilent), Fourier Transform Infrared Spectroscopy (FTIR), analysis, scanning electron microscope (SEM) (JOEL JSM- IT500HR), coupled with energy dispersive X-ray (EDX) spectrometer.
- 2) To determine the effect of different carbon dots on the physicochemical properties of CD@ZIF-8 membrane:
 - i) Prior to the solvothermal synthesis of ZIF-8, the surface of the alumina hollow fibre membrane was modified using 3-(aminopropyl)triethoxysilane (APTES).
 - ii) The modification of the alumina membrane surface was carried out by immersing the alumina hollow fibre membrane in a mixture of ZIF-8 precursors and as-synthesized carbon dots via a direct in situ solvothermal method. To prevent the synthesis solution from entering the lumens of the alumina hollow fibre membrane, both ends were sealed with PTFE.

- iii) The surface morphology of the CDs@ZIF-8 alumina hollow fibre membrane was monitored using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).
- 3) To evaluate the performance of carbon dots ZIF-8 membrane on the removal of lead(II) from the water:
- i) The adsorption of lead(II) was investigated through a batch adsorption study, in which the membrane was immersed in synthetic lead(II) ion solutions. Residual lead levels were measured over time using atomic absorption spectrometry (AAS), and the membrane's adsorption capacity and lead(II) removal efficiency were determined.
 - ii) The potential of the carbon dots–ZIF-8 membrane for filtration was evaluated to determine the water flux and lead(II) removal efficiency.

CHAPTER 2

LITERATURE REVIEW

2.1 Industrial heavy metal pollution

Heavy metal contamination in industrial effluent are severely harmed by the fact that they accumulate in the food chain and cause pollution concerns about the environment by posing a serious threat to aquatic ecosystems, animals, and people (Ibrahim et al., 2020). Heavy metal pollution is a considerably the worst significant problem since it cannot be decomposed by natural processes and remains in soil and sediment, where it is quickly discharged as drains into waterways (Paul, 2017). The wastewater from the industries operations like mining activities, battery manufacturing plants, paper manufacture, the textile and dye industries, and ceramics industry, commonly encountered with hazardous chemicals, particularly heavy metals (Shahbudin and Kamal, 2021). Heavy metal contamination has been reported in numerous nations in the past few years and their concentrations in the water of several other well-known rivers are greater than the legal limit while the contamination is considerably worse in many tiny rivers (Kändler et al., 2017).

The Heavy Metal Pollution Index (HPI) has been widely used by many studies to measure metal pollution in relation to current water quality standards (Ibrahim et al., 2020). Lead (Pb), zinc (Zn), mercury (Hg), nickel (Ni), cadmium (Cd), copper (Cu), chromium (Cr), and arsenic (As) are the most frequently detected metals. Metals and their compounds with an atomic density more than $4 \pm 1 \text{ g/cm}^3$ which include Cu, Zn, Hg, Cd, Pb, Sn, Mn, As, Cr, Co, Ni, Ag, and Al, are often referred to as "heavy metal pollutants" (Qiu et al., 2021).

Despite the fact that certain heavy metals may be identified in low amounts, they are still dangerous (Qasem et al., 2021). As reported by Shahbudin and Kamal (2021) studies, the Klang River, Malaysia also has significant levels of iron, zinc, lead, and cadmium, owing to the presence of former mining ponds, which aided in the migration of heavy metals into the river. In summary, it has been shown by Kořak et al. (2017) that widespread use of heavy metals in industrial processes and intermediary products has resulted in their emissions into the atmosphere from main geological sources, as well as into surface- and ground waters and soils. As a consequence of increased worldwide ecological awareness regarding toxic heavy metals, it has been recognised that there is a need to improve public health and environmental protection as a result of continuing exposure dangers, even in minor daily doses (Kořak et al., 2017).

2.1.1 Lead (Pb)

Pb is a blue-gray, malleable metal that is in the 14th group of the periodic table and it is often utilised in a variety of industrial applications, including electroplating, printing, and the manufacture of dyes, batteries, and paints (Ugwu et al., 2021). According to the Environmental Protection Agency (EPA), there are 129 contaminants that are prioritised, with lead (Pb) being the most serious (Shahbudin and Kamal, 2021). Pursuant to the EPA, Pb is a potential human carcinogen with the potential to impact every organ and system in the human body (Yunus et al., 2020). As discussed above, lead is a well-known metalloid that may be found in large quantities in the earth's crust. Softness, malleability, low melting point, and corrosion resistance are some of the distinctive characteristics of lead, which make it useful for a variety of industries such as batteries, automobiles, paint, ceramics and plastics (Awual, 2017; Awual, 2019). However, these releasing industries' wastewaters are high in lead ions (Pb^{2+}), a harmful contaminant that may raise their concentration in the

environment and last for a long period, causing serious health consequences (Giri et al., 2022).

In fact, the long-term exposure in adults can lead to reduced nervous system performance, as well as weakening in the fingers, wrists, and ankles, minor elevations in blood pressure, and anaemia (Yunus et al., 2020). Qasem et al. (2021) explained the sources of Pb as well as the health risks associated with excessive levels and the permissible limits in drinking water based on WHO (World Health Organization) guidelines. Pursuant to Qasem et al. (2021), Pb could be derived from multiple of sources such as solder, cable wrapping pigments, rust inhibitors, alloys, ammunition, glazes, plastic stabilisers, and lead-based batteries. As far as Pb is concerned, Pb^{2+} salts that are soluble or sparingly soluble in water or soil rapidly infiltrate biological systems and have a substantial impact on living organisms (Giri et al., 2022). Not just that, lead is the most dangerous toxin among the heavy metals, and it is absorbed and consumed in the body in its inorganic form via food, drink, and breathing, which will interact with biomolecules like enzymes and proteins to generate stable bio-toxic compounds, mutilating their structures and preventing them from performing their tasks via bio- reactions (Kořak et al., 2017).

Furthermore, the human body system can be affected by Pb: Immunological system, haematological system, cardiovascular system, and reproductive system and human organ also received negative impacts especially: Bones, liver, kidneys, brain, lungs, and spleen (Qasem et al., 2021). A more detailed account of Pb is given by El- Naggat et al. (2019) which explained that Pb is one of the most dangerous metal ions found in wastewater and has the power to harm the central neurological and reproductive systems, as well as the kidneys, liver, and fundamental cellular processes and brain functioning. The lead poisoning

may also induce the bioaccumulation in bone, which replaces Ca^{2+} and inhibits antioxidant enzymes and increases production of reactive oxygen species (Giri et al., 2022).

The legal limit for Pb in drinking water based on EPA is 15 parts per billion (ppb) (Kinuthia et al., 2020). Allowable quantities of Pb is 10 μg per litre (Qasem et al., 2021). As far as lead is concerned, lead(II) is indeed a non-biodegradable heavy metal that is found in natural water bodies on a regular basis (Chatterjee et al., 2018). To secure human life and the environment, there are regulations in place to limit lead(II) metal concentrations in wastewater of set by the USEPA which included 3 different water environment system. In brief, maximum permissible limit in water (mg/L), in wastewater discharged into public drainage system (mg/L), and in wastewater discharged into inland surface water (mg/L) are 0.01, 1.0, and 0.01 (Afolabi et al., 2021). Short-term exposure to Pb^{2+} (100–120 $\mu\text{g}/\text{dL}$) causes headaches, stomach aches, muscle soreness, exhaustion, and vomiting; however, long-term exposure, even at lower doses (40–60 $\mu\text{g}/\text{dL}$), causes chronic vomiting, lethargy, damage of the brain, convulsions, and unconsciousness (Giri et al., 2022). As a response, it's critical to remove lead from industrial effluents before they're released into the environment.

2.2 Lead (Pb) removal technologies

The present stage of different industrial advancements is leading to an increase in the number of pollutants produced into the environment each year. Large volumes of industrial waste, particularly wastewater tainted with heavy metals like lead (Pb) have been discovered (Kamal and Rafey, 2021). Some of the processes that are becoming popular and being frequently utilised, as well as their challenges and opportunities are explored in the following subsections (Dutta et al., 2021). This part of chapter covers a variety of heavy metal decontamination processes, including adsorption, membrane filtering, and electrolysis.

2.2.1 Electrochemical and electrolysis

In the case of lead(II) removal application, electrolysis is one of the earliest employed water treatment methods and is extensively applied for the general removal of heavy metals from industrial wastewater owing to its simple treatment principles, ease of operation, and capacity to bear the effect of heavy metals in the huge amounts and high concentrations of wastewater (Tran et al., 2017). As explained by Haris et al., (2021), the electrochemical attributes of the contaminant metal are used in the fundamental process of electrolysis in industrial effluent, the heavy metal ions are extracted from the high concentration solution and deposited on the cathode when subjected to an external direct current, leading to the removal of hazardous heavy metals from wastewater. Concurrently, the strongest reducing agent underwent oxidation at the anode. Choumane and Peulon (2021) reported that, electrocoagulation and electrolysis by reduction of soluble ions into metals are two basic electrolytic techniques that may remove heavy metals from wastewater, according to literature research. Besides, the electrochemical treatment is a promising and appropriate technology that requires few chemicals and offers great efficacy, low maintenance costs, quick results, and less effort, which include three different methods: EC (electrocoagulation), EF (electroflotation), and EO (electrooxidation). Interestingly in an electrolytic membrane cell study, copper, chelating agents (EDTA, NTA, and DTPA), and a surface active derivative of DTPA are all electrochemically extracted from alkaline solutions (Eivazihollagh et al., 2019). The electrodeposition of metal ions in the membrane electrolysis cell was used to characterise the recovery process. Furthermore, a cation exchange membrane separated the anode and cathode chambers during treatment to avoid anodic oxidation (destruction) of chelating ligands, allowing for chelating ligand recovery and simultaneous metal collection via electrodeposition.

Recent findings by Choumane and Peulon (2021) also demonstrated that electrochemical treatment is a highly efficient method, capable of removing 99.99 % of lead(II) even at high concentrations. The process rapidly achieves lead levels that comply with environmental regulations ($10 \mu\text{g L}^{-1}$), WHO drinking water standards ($7.2 \mu\text{g L}^{-1}$) and Malaysia's National Drinking Water Quality Standard (NDWQS), which sets the allowable limit for lead at $10 \mu\text{g L}^{-1}$ (Lim et al., 2012). Nonetheless, electrochemical treatment is rarely given much weight in conventional wastewater treatment because of its high cost and energy consumption. However, owing to its effectiveness, it may be a necessary step in the removal of metals from wastewater (Dutta et al., 2021).

2.2.2 Adsorption

When it comes to addressing the environmental problem of metal toxicity, there is always a need for more sophisticated technologies that are both highly effective and inexpensive to eliminate these contaminants (Giri et al., 2022). Adsorption was among the most common and successful ways for the adsorption of various contaminants due to the flexibility of the adsorption mechanism in the operation and design (Awual et al., 2018). Among others promising water remediation techniques (filtration, chemical precipitation and electrochemical methods), adsorption has appeared as one of attractive potential candidates because of its great efficiency, cheap cost, and convenience of use (Tanihara et al., 2021). According to Ahmad et al. (2021) literature, the adsorption process is primarily influenced by chemical structure and porous adsorbents, hydrogen bonding, pore-volume, π - π interaction, acid-base interactions, and active sites emerge throughout adsorbents. Adsorption is a surface phenomenon in which a solution comprising the adsorbate binds to the adsorbent's surface and it can take two forms:

- i) physisorption, where it reversible, weak, endothermic, depends on the surface area, and defined as the adsorbate binds to the adsorbent owing to van der Waals forces, and
- ii) chemisorption is irreversible, selective, exothermic and described as the adsorbate adheres to the adsorbent caused by chemical processes (Hussain et al., 2021). In this form of adsorption, the interaction forces are either ionic or covalent (Ugwu et al., 2021).

As pointed out to the experimental evidence on the material characterisation following the removal studies shows that Pb^{2+} removal is mostly accomplished by adsorption (Tanihara et al., 2021). In addition to its many advantages, adsorption is becoming more popular because of its cost-effectiveness and efficiency. The use of environmentally friendly sorbents, cost-effectiveness, ease of regeneration, and low energy demands as well as the vast variety of proven adsorbents obtained from agricultural and industrial wastes which could be used (Gupta et al., 2020). Adsorption is a mass exchange approach that involves moving a liquid (molecules move out of the solution) to a solid's surface and then allowing chemical and physical interactions to bind the two together (Hassan et al., 2020). In others literature from Ugwu et al. (2021), adsorption is described as a physicochemical treatment procedure that is ideal for getting rid of undesirable and frequently hazardous compounds as well as the adsorbates connect to the adsorbents in a more or less reversible reaction throughout this phase. The review presented by Dutta et al. (2021) thus far supports the idea that adsorption is a viable approach for adsorbing metals since it offers a lot of surface area. A solid phase called as adsorbent is passed through the wastewater containing metals in this process and the selected metals are adsorbed on the surface and then can be collected individually from there (Dutta et al., 2021). It is also a reversible process, since the adsorbents may be

replenished by desorption operations, which is considered cost effective (Qalyoubi et al., 2021b). Apparently, adsorption is viewed as a mass transfer mechanism, in which a material is transported from the liquid phase to a solid surface by physical and/or chemical interactions (Vo et al., 2020). The adsorption mechanism can be found through different interaction as showed in Figure 2.1.



Figure 2.1: Heavy metal removal mechanism by adsorbent (Shakoor et al., 2020; Liu et al., 2020)

2.2.2.1 Adsorbent materials

Two critical factors in the selection of efficient adsorbents for the removal of heavy metals are cost-effectiveness and specialised applicability, which should be considered together (Gupta et al., 2020). The shape and chemistry of the adsorbents utilised determine their effectiveness (Qalyoubi et al., 2021b). Adsorbent selection is the most critical aspect of adsorption technology. Accomplishments such as high specific surface area, quick adsorption rate and short equilibrium period are necessary for an excellent adsorbent

material (Qiu et al., 2021). Agricultural waste, industrial by-products, and natural substances could all be used to make the adsorbent (Dutta et al., 2021). Agricultural waste such as peanut shells, plum seeds, olive pips, and pine sawdust are often low-cost bio-adsorbents (Bhanjana et al., 2017; Durán-Jiménez et al., 2019; Ghaedi et al., 2018; Košak et al., 2017). Unfortunately, there had been a lack of reusability, which posed a new disposal issue (Awual, 2019). In order to remove lead from polluted water, activated carbon and other adsorbent materials are commonly employed. Although activated carbon is utilised on a large scale, it has a number of drawbacks, including high cost, a limitation of regenerability, and a small surface area (Bhanjana et al., 2017).

Researchers are currently developing new non-toxic, durable, and appropriate materials for high adsorption of certain metal ions from aqueous solutions. Due to their high surface-to-volume ratio, large pore volumes, and excellent mechanical strength, nanomaterials have been proposed as promising adsorbents for monitoring and removing metal ions in water treatment applications (Abbas et al., 2018). Porous silica material has been proposed as a popular and effective material in the field of pollution remediation and metal ion recovery, such as radionuclides, heavy metals, rare-earth elements, and precious metals, due to its remarkable characteristics, which include chemical stability and large pore structures and also well functional based materials (Awual, 2019).

Furthermore, ligand-anchoring conjugate compounds are attractive for environmental applications due to their enhanced binding properties. The abundant hydroxyl groups on porous silica surfaces allow covalent interactions with organic ligands such as amine, thiol, carboxyl, and phosphonic acid groups, followed by co-condensation or non-covalent hydrogen bonding interactions (Awual, 2019). The organic compound grafting material may have exceptional functionality in adsorbing lead(II) from wastewater based on

colour change and eco-friendliness, allowing for large- scale application of actual waste sample remediation (Awual et al., 2019).

Adsorbents may be found in all solids such as activated carbon, silica gels, zeolites, and activated alumina are the most often utilised in the industrial sector. Because of their highly developed porous architectures and huge specific surface area, these materials exhibit high adsorption capacity (Ugwu et al., 2021). Reduced costs might help expand the adsorption technique's usability (Karri and Sahu, 2018a). As a result, low-cost and readily available adsorbents must be explored (Karri and Sahu, 2018b). Researchers have thus emphasised the relevance of zeolites as a low-cost and efficient adsorbent for water/wastewater heavy metal retention. Alkali or earth alkali metal zeolites ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot n\text{H}_2\text{O}$) are aluminosilicate crystals comprising crystal water, 20 to 50 % of which is composed of voids (Taamneh and Sharadqah, 2017). Their application in adsorption processes is attributed to several key advantages, including low cost, high cation exchange capacity, non-toxicity, and strong affinity for negatively charged ions at low temperatures (Hong et al., 2019).

2.2.3 Membrane separation technology

Membrane technology has been developed in past few decades, and there are now more types of materials available for membrane preparation. For membrane preparation, high molecular weight organic polymers, alumina, and natural minerals might all be employed. Membranes are classified as organic or inorganic based on the materials used to make them (Liang et al., 2021). In wastewater treatment and desalination, organic membranes are often utilised (Chu et al., 2020; Li and Zhang, 2017). However, membrane technologies still face significant challenges related to the trade-off between permeability and selectivity, as well as issues such as fouling and scaling, which hinder long-term

operation (Goh and Ismail, 2018). In contrast, ceramic membranes offer superior thermal stability, mechanical strength, chemical resistance, longer operational lifespan, and enhanced anti-fouling properties compared to organic membranes. As a result, ceramic membranes are more suited to applications involving high temperatures and corrosion, such as flue gas moisture recovery, gas purification, and desulfurization wastewater treatment. More crucially, inorganic membranes are less prone to bacterial breakdown, which is the primary cause of biodegradation in most polymeric membranes (Liang et al., 2021).

Heavy metal ions have been extracted from wastewater using membranes as a filter and extraction method due to technological improvements in membrane research (Qasem et al., 2021). At the cellular level, each action necessitates a distinct layer that serves as a filter or separates water from contaminants (Saravanan et al., 2021). There is a range of membranes depending on the materials they are made from, such as membranes of polymeric polymer, membranes made of ceramics. In addition to the ion exchange membrane, a liquid membrane is also an option (Samaei et al., 2018). Ceramic membranes have been widely employed for a variety of applications, including industrial wastewater treatment, due to their chemical resistance, thermal stability, and toughness (Asif and Zhang, 2021). Ceramic membranes used in industry nowadays are often multi-layered asymmetric structures made up of one or more ceramic materials.

Ceramic membranes have a number of advantages, including the fact that they do not swell throughout solvent filtration, can endure high temperatures and backwashing pressure, and are insensitive to cleaning chemicals and oxidants (Samaei et al., 2018). Although ceramic membranes offer several advantages, such as thermal and chemical resistance, polymeric membranes continue to dominate the water and wastewater treatment industry due to their lower production cost and ease of fabrication (Asif and Zhang, 2021).

Membrane processes commonly used in these applications include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), forward osmosis (FO), and reverse osmosis (RO) (Saravanan et al., 2021). Ideally, membranes should exhibit consistent flow velocity without dead zones, be easy to clean and maintain, cost-effective, structurally compact, and exhibit minimal fluid resistance (Saravanan et al., 2021).

As explained by Qasem et al. (2021), microfiltration is driven by low pressure, with membrane holes in the range of 0.1–10 μm which utilises a microporous membrane to remove micron-sized particles such as bacteria and viruses, protozoa and contaminants from a solvent, fluid, or solution. Owing to MF's poor capacity to remove heavy metal, its usage in this application has received little consideration and has predominantly been used in pharmaceutical and biological industries. Similarly to microfiltration, ultrafiltration (UF) is based on particle capture or size exclusion and is described by the molecular weight cut off (MWCO) of the membrane which is specified in cross-flow or dead-end mode that are applied in various sectors of the ultrafiltration membrane (Youcai, 2018). UF membranes are frequently utilised to eliminate viruses, microorganisms, colour pigments, as well as certain natural organic colloids, and feature pores between 10 and 100 nm in diameter (Dehdashti et al., 2020). In addition, UF is a more energy- efficient technique than reverse osmosis (RO), which demands a much greater transmembrane pressure and hence a much bigger energy demand (Adam et al., 2019). Water desalination, drinking water manufacturing, brackish water treatment, and wastewater treatment all require RO membrane innovation (Dehdashti et al., 2020). The benefits of a RO membrane include high water permeability and salt rejection, as well as compliance with the most strict public health, environmental, and separation rules (Zeng et al., 2019). In the context of heavy metal removal, RO is often primarily used to treat huge volumes of brackish groundwater and may

be applied to efficiently remove metallic ions without the use of secondary chemicals (Yang et al., 2019).

Forward osmosis (FO) is a type of osmosis that uses a membrane to maintain a balance of selectivity and penetrated water flow (Qasem et al., 2021). FO is energy- efficient since it does not need hydraulic pressure and it is frequently utilised in wastewater treatment due to environmentally safe, easy to clean and minimal fouling (He et al., 2020). Nanofiltration (NF) membranes are intended to remove contaminants smaller than 10 nm and are particularly fit for water softening purposes (Adam et al., 2019). NF membrane technology in water and wastewater treatment has several advantages, including the removal of divalent ions such as heavy metals without the use of secondary chemicals, the ability to treat waters containing multiple types of heavy metals, an automated process, and continuous water treatment (Dehdashti et al., 2020).

2.3 Type of membrane separation technology

The four most common forms of membrane configurations are spiral wound plate and frame, tubular, and hollow fiber modules (Ezugbe and Rathilal, 2020). Table 2.1 provides an overview of some of the membrane configuration's characteristics.

Table 2.1: Some of the fundamental characteristics of membrane components (Ezugbe and Rathilal, 2020).

Characteristics	Hollow Fiber	Plate-and-Frame	Tubular	Spiral wound
Possibility of a foul	Very High	Moderate	Low	High
Manufacturing Costs in Relation	Low	High	High	Moderate
Ease of Cleaning Performance	Poor	Good	Excellent	Poor
Packing Density (m^2/m^3)	492–4924	148–492	20–374	492–1247

2.3.1 Hollow fibre (HF) configuration

Hollow fibre membranes are often made using the conventional wet spinning technique, which has the benefits of nature technology and efficient membrane separation. However, these hollow fibre membranes may not be adequate to meet the proper application due to their weak mechanical properties and poor permeability stability. The membrane filaments were exposed to long-term high-pressure flow, and following high water flow and regular cleaning might cause significant damage to the membrane and even lead it to disintegrate (Chen et al., 2019; Chu et al., 2020). In earlier work by Ji et al. (2019), researchers effectively constructed new hollow fibre NF membranes with dense-loose structure in a single step method of non-solvent induced phase separation with no post-treatment, where it applied for treating simulated textile wastewater. The optimised membrane demonstrated a high dye rejection of 99.9%, while these types of membranes were readily damaged and compacted, affecting the permeability stability of the membrane sequentially (Ji et al., 2019). Today, one of the strategies for improving the mechanical

properties of hollow fibre membranes with high permeability stability is to add supporting reinforcement (Chu et al., 2020).

The preparation of reinforced hollow fibre membranes has been the subject of a number of extensive review publications. For example, Liu et al. (2013) used a coating process to fabricate homogeneous reinforced polyvinyl chloride (PVC) hollow fibre membranes, which included a coating layer and matrix. Another study by Fan et al. (2015), described homogeneous braid reinforced cellulose acetate (CA) hollow fibres with a CA separation layer and CA layer tubular hollow braid. These studies revealed that the membrane's mechanical properties had improved, along with its permeability. Despite this, the hollow fibre membrane's lateral pressure resistance remains a challenge due to the membrane's ease ability to bend and compact under relatively high operating pressure (Chu et al., 2020).

Herein, hollow fibre membranes offer a higher surface area to volume ratio and a higher packing density than flat sheet and tubular membranes and may also be self-supporting which consequently no longer necessary the use of spacers during module construction (Gao et al., 2020a). Single adsorptive membranes (AMs) with hollow fibers are noteworthy in that they are flexible, economical, convenient, quickly adsorb at low pressure, and recycle continuously (Vo et al., 2020). Regardless closed or open end in a pressure vessel, this module type stores a bundle of hollow fibers and comprise of a porous non-specific support layer of roughly 200 μm and more than 40 nm diameter of active layer where it is the membrane itself, however it requires support to endure hydrostatic pressure (Ezugbe and Rathilal, 2020). In fact, hollow-fiber ceramic membranes are ideally suited for wastewater treatment among the various geometries. This is because, when compared to flat-sheet ceramic membrane modules, hollow-fibre ceramic membrane modules offer higher

mechanical strength and packing density, as well as improved handling capability against high crossflow velocities (Asif and Zhang, 2021). Figure 2.2 showed the example of ceramic hollow-fibre membrane.



Figure 2.2: Ceramic hollow–fibre membrane (Samaei et al., 2018).

Based on their mode of operation, hollow fibre membrane modules are generally classified into two types: inside–outside and outside–inside configurations. Mentioned by Rahimpour et al. (2018), the inside-outside HF (bore-side feed) is described when the permeate is formed on the fiber's exterior wall when the hot feed entering inside the hollow fibre whereas outside- inside HF (shell-side feed) defined as the feed flows through the fiber's outer wall, while the permeate flows through the inside. The shell-side feed type is ideal for high pressure purposes (up to 70 bar), meanwhile the bore-side feed version is suited for low to medium pressure purposes (Ezugbe and Rathilal, 2020). The hollow fibre membrane application is seen in Figure 2.3.

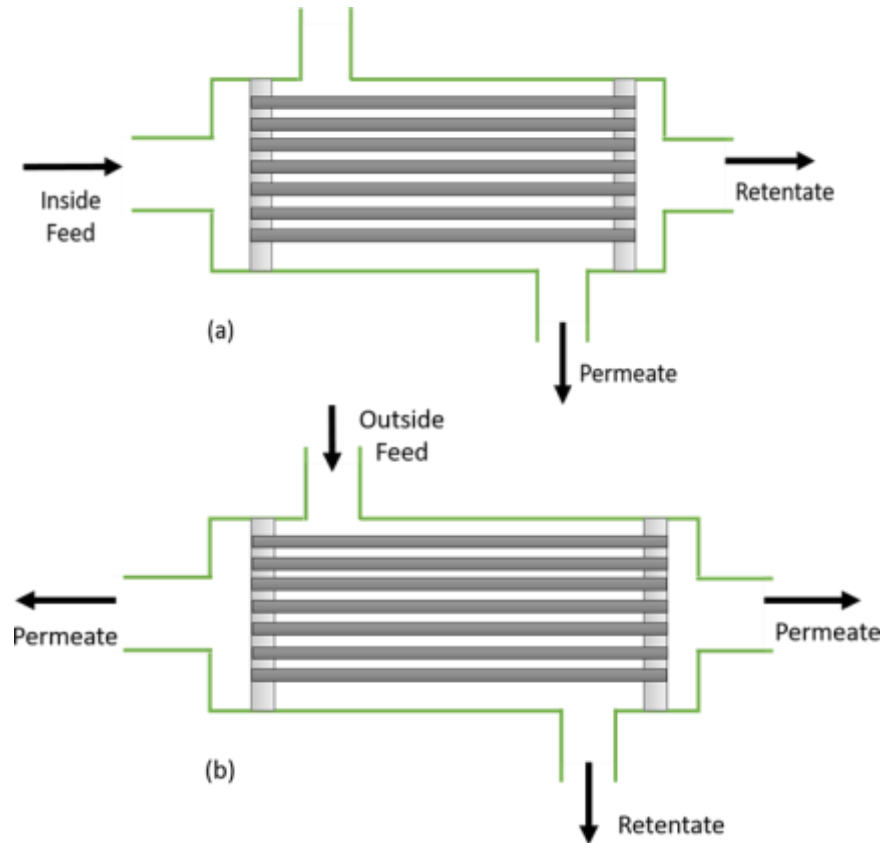


Figure 2.3: (a) The inside-outside HF (bore-side feed) and (b) the outside-inside HF (shell side feed). Adapted from (Ezugbe and Rathilal, 2020)

2.4 Ceramic membrane

Ceramic membranes have been reported to be thermally stable, chemically stable, and have a long lifespan, making them suitable for industrial wastewater treatment (Samaei et al., 2018). Asymmetric structures are common in ceramic membranes used for water and wastewater treatment, with a thin selective layer, intermediate layer(s), and permeable supporting layer. It is necessary to keep in mind that the thin selective layer achieves separation, while the intermediate and support layers give selectivity, as well as stability and strength (Qiu et al., 2017). The ceramic membrane consisted of 3 layers as illustrated in Figure 2.4.

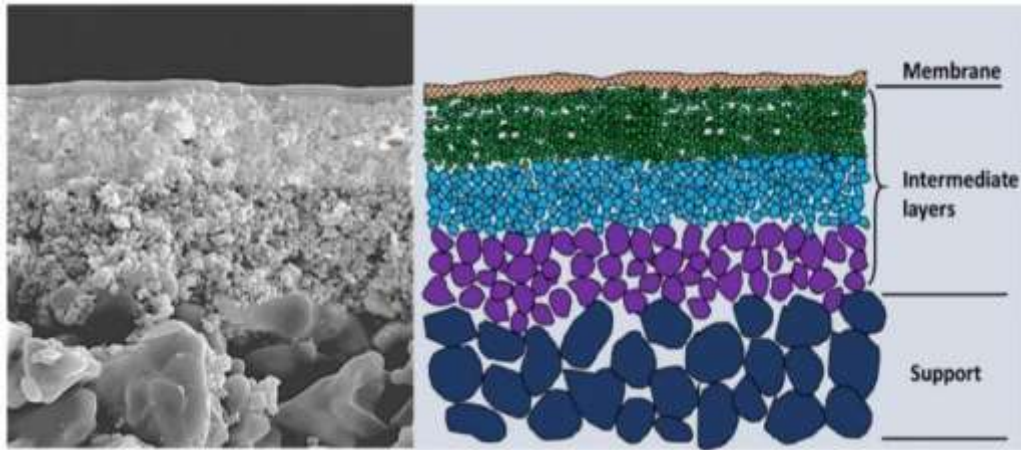


Figure 2.4: A cross-sectional diagram of a ceramic membrane. Adapted from (Qiu et al., 2017).

The composite ceramic membranes, in particular, can be customised to obtain desired selectivity and characteristics, making their production complicated. Ceramic membranes' geometries and configurations are determined by the supports, which allow them to be either cylindrical (i.e., hollow-fibre and multichannel tabular) or flat (i.e., flat-sheet) with varying packing densities (Asif and Zhang, 2021). As matter of fact, the ceramic unit outperforms polymeric membranes in terms of durability, chemical, mechanical, and thermal stability, bacteria resistance, back flushing capability, and cleaning and sterilisation ease. Nevertheless, this technology still faces obstacles, such as lowering capital and manufacturing costs, improving selectivity and antifouling qualities, increasing packing densities, and translating experimental research findings to large-scale applications (Samaei et al., 2018).

Moreover, as reported by Asif and Zhang (2021), in the past study, ceramic membranes have been coated or modified with diverse (nano) materials such as TiO_2 , Ag, and MnO_2 in recent attempts to increase antifouling, pollution removal, and disinfection effectiveness. In general, Aluminum (Al), zirconium (Zr), silicon (Si), and titanium (Ti)

oxides are regularly utilised materials for the separation layer during the manufacturing of ceramic membranes (Xing, 2017). Alumina ceramic membranes are more widely available than ceramic membranes and comprised of other materials, such as silicon carbide, due to their favourable price-to-performance ratio. This can also be ascribed to alumina's cheaper cost compared to its alternatives (Asif and Zhang, 2021). Interestingly, the most often used ceramic membranes are made of metal oxides such as alumina, titania, zirconia, and others, with alumina being the most prevalent (Azaman et al., 2021).

2.5 Ceramic membrane preparation method

2.5.1 Sol gel method

Sol-gel is a process of producing tiny particles in a liquid medium and then solidifying them after coating/shaping to produce homogenous layers/structures of fine particulates after drying and heat treatment. Metal-organic compounds (alkoxides) or metal salts may be used as starting components for sol-gel. Appropriate precursors are reacted through polymeric or colloidal pathways. The pathways include (i) the creation of polymeric or colloidal particles in liquid medium (sol formation), (ii) the construction of a network among these particulates (gel formation), (iii) drying of the gel, and (iv) heat treatment. In the reaction pathways, acidic or basic catalysts may be utilised, and via acidic catalysts pathways; it can generate finer particles, resulting in a finer microporous structure at the last part of the membrane manufacturing process (Erdem, 2017). The hydrolysis and condensation processes are included in the sol-gel. Metal alkoxide precursors ($(M(OR)_n$ which M are either Zr, Ti, Al, Si, etc. and R is an alkyl group) are employed reacted with water in these condensation synthesis processes (Moattari and Mohammadi, 2020).

This approach offers several benefits, including homogeneous pore distribution and excellent purity products despite the low temperature required (Ağtaş et al., 2021). The

particle size may be commonly modified using the sol-gel process (Moattari and Mohammadi, 2020). The frequency of condensation and hydrolysis reactions dictate the speed and size of particle production in the sol. Some additives (such as acetyl acetone) may be used to delay condensation and inhibit the production of larger particles in the sol (Erdem, 2017). However, the presence of cracks while drying might be regarded as a drawback (Ağtaş et al., 2021). The sol-gel process is used in a lot of instances of ceramic membrane preparation. Li et al. (2019) reported the resulting sol-gel derived membrane characterized by silicon carbide as the substrate layer and zirconia as the separation layer. The morphology of the substrate, the characteristics of the sol, and the heating and drying treatment conditions are essential elements that determine the pore structures of the separation layer formed by the sol-gel method. The zirconia layer may fracture at high temperatures due to water evaporation-induced shrinkage or stress-induced phase change from the tetragonal to the monoclinic phase. Li et al. (2019) studies are consistent with the explanation of Kwaśny et al. (2018), whereas the surface tension between them makes large monolithic structures harder to prepare materials and leads to gel cracking, collapse, and shrinking which is relatively typical in sol-gel processing. To address this issue and avoid fractures during drying, organic binders are added to the solution, and these molecules are removed from the membrane during heating (Ağtaş et al., 2021). Unfortunately, in the sol–gel processing of ultra-high temperature ceramics, powders and broken pieces are often formed, as illustrated in Figure 2.5.

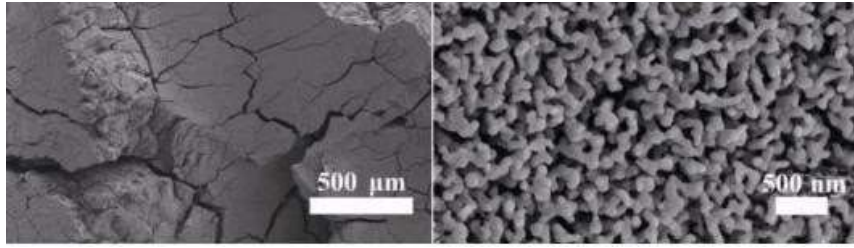


Figure 2.5: A sol–gel produced zirconium carbide–silicon carbide composite heated at 1500 °C for 1 hour at low and high SEM images magnification (Li et al., 2019)

2.5.2 Slip casting method

Slip casting is a simple and cost-effective way of fabricating ceramic membranes. Due to the possible excellent controllability over the ceramic phase degree of dispersion and the porous material's microstructure, it is one of the most widely utilized fabrication processes at the industrial level (Ewis et al., 2021). This approach has the benefit of being able to shape complex geometries and irregular designs while still obtaining great material uniformity (Issaoui and Limousy, 2019). In general, this process typically includes mixing the ceramic powder with demineralized water, organic binders, and chemical deflocculants in a slurry. The purpose of chemical deflocculants are required to sustain the slurry's colloidal stability (Wiecinski and Wieclaw-Midor, 2020). The slurry is then loaded into a porous mold, where capillary suction pressure induces the solvent to permeate through the pores and create a layer on the interior mold surface, which consolidates afterwards (Ewis et al., 2021). It corresponds with Ağtas et al. (2021) explanation where the slurries must be movable and have a large solid content in order to be poured. Upon pouring the slurry into the casting mold, the solvent is drawn out of the slurry by capillary force, forming a solid layer with a specific strength and thickness. For the sintering process, this solid layer is demolded. The final product's qualities are determined by the binder concentration, particulate size in the slurry, time, and temperature.

The excess solvent is then removed from the mold by a slow drying process, resulting in a longer casting period. The membranes formed via slip casting have a high wall thickness that is difficult to manage. The thick membrane wall may be a negative for membrane distillation desalination performance since it increases vapour transport resistance and hence lowers flow (Tai et al., 2020). This also accords with another review Azaman et al. (2021), which showed that the method entails a lengthy drying process, this approach sometimes necessitates a long casting period. The possible disadvantages are while preparing a slurry to get the desired end result, the ratio of powder combination to water employed should be correct. Furthermore, the wall thickness is difficult to manage during the drying stage's consolidation, and is typically thick (Azaman et al., 2021). The illustration of slip casting method can be observed as Figure 2.6 and 2.7.

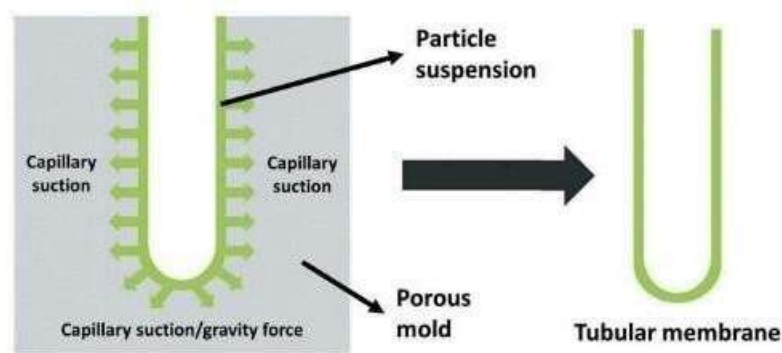


Figure 2.6: Capillary suction and gravity force draw the solvent into mold's pores and a slip particles layer simultaneously formation on mold surfaces (Tai et al., 2020)

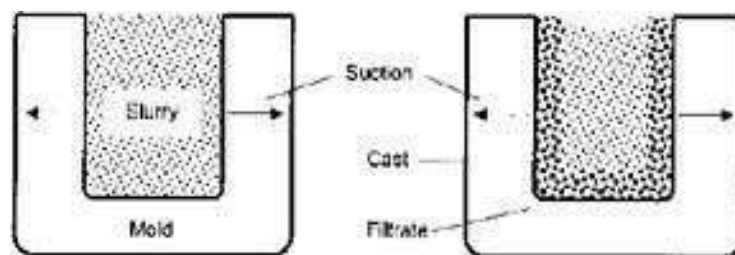


Figure 2.7: The solidified layer also known as a cast, develops on mold's wall is shown in the diagram (Azaman et al., 2021)

2.5.3 Phase inversion and co- sintering method

In comparison to existing approaches, the combined phase inversion and sintering process has been shown to be a promising method for the manufacturing of ceramic membranes. Flat sheets, hollow fibre, and tubular ceramic membranes have all previously been produced using phase inversion and sintering (Alias and Sufianasuri, 2021). The asymmetric ceramic membranes are made in a single fabrication step using this approach because only one heat treatment is required. Preparing a suspension of ceramic particles, an organic solvent, a polymer binder, and water is necessary for this method. The ceramic particles are immobilised by spinning or casting, according to the shape, due to phase inversion created by the interaction of solvent and non-solvent. Finally, all organics are eliminated from the membrane precursors, and the mechanical characteristics of the membrane are enhanced (Alias and Sufianasuri, 2021). Porous ceramic membranes have been fabricated by combining phase-inversion technology with conventional ceramic forming methods such as extrusion, spinning, and tape-casting. Numerous studies have successfully produced hollow-fibre structures using ceramic powders like alumina and yttria-stabilised zirconia (YSZ). In these preparations, polyethersulfone (PESf) dissolved in solvents such as N-methyl-2-pyrrolidone (NMP) or N,N-dimethylformamide (DMF) served as the binder solution, while water acted as the coagulating bath (Nishihora et al., 2018).

Hydrophobic metakaolin-based flat sheet membrane has been developed by Zewdie et al. (2022) via phase inversion and sintering technique and modified through 1H,1H,2H,2H- perfluorooctyltriethoxysilane grafting agents. It has been shown that the shrinkage of the metakaolin-based flat sheet membrane tends to increase as the sintering temperature rises. SEM images of the influence of sintering temperature (varying from 1,200 to 1,500 °C) on the membrane surface morphology of metakaolin based flat sheet membrane are shown in Figure 2.8.

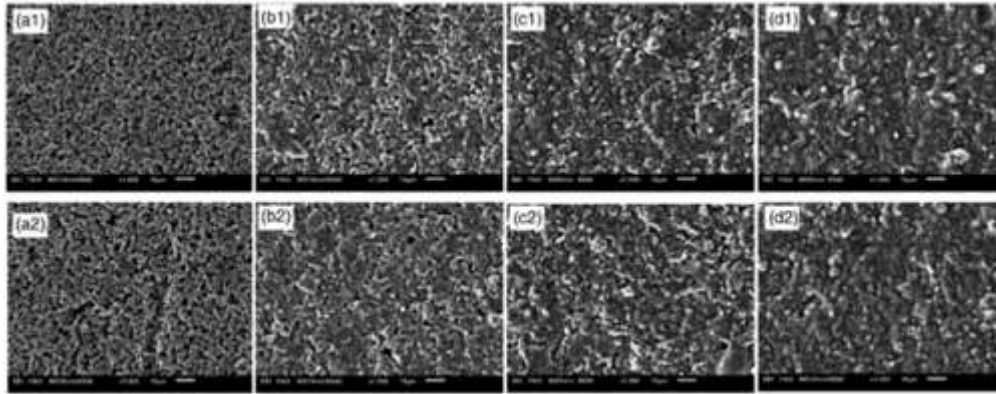


Figure 2.8: SEM image of the surface of the metakaolin-based flat sheet ceramic membrane. (a1, a2) sintered at 1,200 °C, (b1, b2) sintered at 1,300 °C, (c1, c2) sintered at 1,400 °C, and (d1, d2) sintered at 1,500 °C for 4 h. (a–d) Unmodified membrane, (a1–d1) modified membrane (Zewdie et al., 2022)

The membrane's surface morphology was determined to be homogeneous and defect-free. At 1,200 °C, the sintered membrane had a porous structure and an evenly dispersed porosity. Small pores disappear and a less porous structure was created at higher sintering temperatures but sintering at 1,500 °C produced the strongest membrane with a very dense structure and restricted grain and non-interconnected pores. This might be because the

particles clump together and form structure. In other words, the porosity of the membrane has reduced as the sintering temperature of the membranes has increased.

As reported by the literature of Yu et al. (2020), oxide ceramic membranes, such as Al_2O_3 , SiO_2 , ZrO_2 , TiO_2 , and composites, typically feature an asymmetric multi-layered structure associated with macroporous ceramic support and afterwards various produced intermediate layers for steadily reducing the pore sizes. As a result, fabricating oxide ceramic membranes demands several coating-sintering operations, each of which is simultaneously time and energy consuming for industrial oily wastewater treatment become more costly. Therefore for the preparation of ion hollow fibre ceramic membranes, a combination of phase inversion and sintering has been favoured among the many fabrication procedures (He et al., 2019). Unlike phase inversion, which is utilised to make polymeric membranes, this method used a ceramic-dominant mixture with proper ceramic powders as the main component and the polymer as a binder. The polymer was burned off during the subsequent sintering process, resulting in porosity. Asymmetric ceramic membranes can be made in a single step utilising the phase inversion/sintering approach, which saves time and money. This process is typically used to create hollow fibre ceramic membranes with a high surface-to-volume ratio and increased mechanical strength (Yu et al., 2020).

2.6 Adsorptive membrane

Many conventional treatment procedures have been investigated and utilised throughout the years. Nevertheless, current research has focused on developing cost-effective and efficient water treatment technologies that may overcome the limits of conventional methods. This drew attention to adsorptive membranes, which may remove a variety of developing toxins that pose a health risk to humans and aquatic creatures (Qalyoubi et al., 2021b). Adsorption, sieving, and electrostatic phenomena are the three

fundamental concepts of membrane technology while the adsorption mechanism in the membrane separation application is based on hydrophobic interactions between the membrane and the solute (analyte) (Nqombolo et al., 2018). Adsorptive membranes (also known as modified membranes) provide a number of benefits, including a high removal rate and efficiency, low operating pressure, high permeability flux, regeneration, optimal reusability, a low footprint, and minimal space requirements (Huang and Cheng, 2020).

In light of this positive influence, different adsorptive membranes such as polymeric membranes (PMs), polymerceramic membranes (PCMs), electrospinning nanofiber membranes (ENMs), and nano-enhanced membranes (NEMs) are discussed in Table 2.2.

Table 2.2: Heavy metal removal with AMs has been the subject of several articles (Vo et al., 2020)

Adsorptive Membranes	Adsorbents	Heavy Metal Ions	Removal Efficiency (%)	Max. Adsorption Capacity (mg/g)	References
ENMs	Poly(vinyl alcohol) (PVA)	Cu^{2+}	-	66.5, 33.6	(Ullah et al., 2020)
	Nanocrystals/Chitosan/Polyvinyl Alcohol Nanofibrous Films (CNC/CTS/PVA SH)	Pb^{2+}	39.4, 44.8	23.9, 10.0	(Wang et al., 2018)
	Thiol-functionalized cellulose (TC) membrane	Cu^{2+} , Cd^{2+} , Pb^{2+}	4.9, 4.6, 2.2	94.3, 161.3, 357.1	(Choi et al., 2020)
	Ploy(acrylonitrile) Chitosan (PAN/CTS)	Pb^{2+} , Cu^{2+}	51.1, 52.9	484.1, 323.5	(Alharbi et al., 2020)
NEMs	Ploy(acrylonitrile) Metal Oxide Chitosan (PAN/MO/CTS)	Pb^{2+}	90.0, 85.0	158.2, 182.5	(Alharbi et al., 2020)
	Chitosan Poly(vinyl alcohol) Zeolite (CTS/PVA/Zeo)	Cd^{2+} , Pb^{2+} , Hg^{2+}	78.5, 80.0, 55.5	296.7, 213.8	(Habiba et al., 2017)
	Zr based metal-organic frameworks (Zr MOFs)	Cu^{2+}	6.0	1.8	(Wang et al., 2018)
PMs	Chitosan Poly(vinyl alcohol)	Cd^{2+} , Cu^{2+}	74.8,	112.1,	(Saheb Jamee et al., 2019)
	Poly(ethyleneimine) (CTS/PVA/PEI)	Ni^{2+}	57.4, 50.3	86.1, 75.5	
PCMs	Polyaniline (PANI)/bentonite (PANIB)	Ni^{2+} , Cu^{2+}	70.0	51.5, 48.5	(Liu et al., 2017)

As indicated previously, microfiltration (MF) and ultrafiltration (UF) are known to remove only certain viruses and suspended solids, whilst nanofiltration (NF) and reverse osmosis (RO) potentially remove heavy metal ions and fluorides but with fouling concerns and large operating pressure (Qalyoubi et al., 2021b). As an outcome, a combination of membranes and adsorption techniques has emerged to overcome some of the limitations encountered when the prior technologies were utilised separately and to leverage the benefits of both (Chong et al., 2019). This was also supported by Shokri et al. (2021) where they stated that compared to nanofiltration and reverse osmosis, adsorptive membranes do not require high transmembrane pressure (TMP), making them a more energy-efficient choice. Moreover, adsorptive membranes have pore sizes ranging from those typical of nanofiltration to microfiltration (Huang and Cheng, 2020).

A descriptive explanation regarding the adsorptive membrane mechanism by Qalyoubi et al. (2021b) displayed that there are two primary methods for removing solutes from wastewater using adsorptive membranes: i) rejection and ii) adsorption. When water-containing solutes come into contact with the membrane's active layer, the molecular sieving occurs to reject any solutes larger than the membrane's pore size. Smaller solutes will penetrate through the active layer and approach the support layer, which serves as an adsorption material microspheres. They will subsequently interact to form a tight internal spherical complex, resulting in a filtered water permeate from the adsorptive membrane that meets the requisite standards (Zhang et al., 2018). Through electrostatic interaction, heavy metal ions from wastewater could well be absorbed via charged inorganic materials introduced in the membrane (Shokri et al., 2021).

As reported by Huang and Cheng (2020), ions and molecules have a strong affinity for adsorptive membranes. As a result, it was also known as an "affinity membrane." They

may chelate (or complexation or ion exchange) to combine ions, therefore they are indeed also known as chelating membranes, complexation membranes, and ion exchange membranes. As most adsorbents, nonetheless, are unable to adsorb both positively and negatively charged heavy metal ions at the same time pursuant to (Shokri et al., 2021). Functionalizing raw adsorbents or creation of nanocomposites are two viable ways for enhancing the simultaneous adsorption of cationic and anionic heavy ions (Shokri et al., 2021).

2.6.1 Adsorptive membrane for lead(II) removal

Adsorptive membranes defined as porous membranes that can be enhanced to contain reactive functional groups such as -NH_2 , $\text{-SO}_3\text{H}$, and -COOH groups on their external and internal surfaces, through ion exchange or surface complex formation (Qalyoubi, et al., 2021a). These functional groups are required for metal ion bonding and are consequently eliminated from solution when the membrane surface is contacted, despite of pore diameters bigger than the metal ion size (Adam et al., 2019). The ion exchange process happens when the adsorbent has active sites containing an electric charge or free electrons, during which the adsorbent and the substance interact electrostatically (Qalyoubi, et al., 2021a). To fully comprehend the process of heavy metal removal by adsorptive membranes, it is indeed important to realise that their interfaces are charged by adsorption and ionization, since the adsorbent may include charged ionic functional groups. One of the example of adsorptive membrane for lead(II) removal is cellulose acetate (CA)/polycaprolactone (PCL) reinforced nanostructured membrane which successfully enhanced increasing trends of the lead(II) adsorption (Aquino et al., 2018). Based on Aquino et al. (2018) study, the combination of 10% PCL developed the of pure CA adsorption capability from 43.96 mg Pb^{2+} /g membrane of pure CA into 70.50 mg Pb^{2+} /g of PCL doped fibrous membrane. On other hand, to be illustrated, mixed matrix polymer membrane which is a novel polyvinyltetrazole-grafted

resin displayed possible highest adsorption capacity for lead(II) (1.52 mmol/g) with a strong preference for lead(II) ion over other ions at pH 5.0 (Qalyoubi, et al., 2021a). Another literature showed that Pb ions was removed from waste water using a polyethylenimine-grafted gelatin sponge and had removal rates of 89.9% efficiency correspondingly (Khulbe and Matsuura, 2018). Many research have looked into the use of nanoparticles as membrane fillers in the adsorption of heavy metal ions from aqueous systems, and Table 2.3 summarizes their unique properties based on the information provided by the authors.

Table 2.3: Nano-adsorbent properties in removing lead(II)

Nano-adsorbents	Unique Properties	Capacity of Adsorbent	Operational Circumstances	References
Graphene Oxide	Distinctive Physicochemical properties	50 mg g ⁻¹	pH: 6, Temperature: 298K, initial concentration of 25 mg/L of lead(II) with aqueous solution	(Peng et al., 2017)
Metal oxides and MOFs	Outstanding performance in removing lead(II)	40-313 g g ⁻¹	pH: less than 6, aqueous solution with deionized water	(Wen et al., 2018)
Bacterial cellulose (BC) based composite membranes embedded with magnesium oxide nano-adsorbents (MgO/BC)	The nano-adsorbent is strongly bonded with the bacterial cellulose nanofibers.	9.6 mg L ⁻¹	A sheet of a multi-component BC composite membrane (UiO-66/MIL-88B/MoS ₂ /MnO ₂ /MgO/BC) treated in 20 mL of a mixed solution containing multiple pollutant.	(Gu et al., 2021)
Empty fruit bunch (EFB) - activated carbon	Modification of environmental application EFB residue for the pollutant removal	2.24 mg L ⁻¹	Optimum reaction condition: 10 g/L of EFB-activated carbon, pH 1.0 and 15 min as contact time	Elias et al., 2021).

Table 2.3: continued

Molybdenum disulfide/reduced graphene oxide (MoS ₂ /rGO) composites	Chemical and monolayer adsorption (surface complexation and electrostatic interactions.)	84.16 mg ⁻¹	pH: 5.0 and Temperature: 298.15 K,	(Du et al., 2017)
Gamma-Al ₂ O ₃ nanoparticles	No significant change in adsorption percentage of lead by increasing the amount of adsorbent.	7.08 mg ⁻¹	pH: 5.0 and the contact time: 20 min	Tabesh et al., 2018)

2.7 Metal organic framework (MOF)

MOFs are commonly made by reticular synthesis, which involves firmly bonding metal ions to organic linkers (Qasem et al., 2021). MOFs were also crystalline porous materials with a crystal structure made up of metal ions or clusters that are linked together by rigid organic ligands to form one, two, or three- dimensional structures (Nagarjun and Dhakshinamoorthy, 2019). The almost similar definition of MOFs exist in the literature from Hoop et al. (2018), where they explained that MOFs are a type of porous material composed of inorganic metal ions (or clusters) that are linked to organic ligands. MOFs have micropores (tiny holes) that are unavailable to a certain targeted metals and in contempt of their intriguing characteristics and strong capacity to remove heavy metal ions, many of them have poor water stability (Qasem et al., 2021). MOFs possess many interesting features, including high surface area, excellent porosity, tunable pore structures, ease of functionalization, and increased availability of chelating sites. They also offer diverse structural topologies, adjustable architectures, good chemical stability, and well-ordered p-

columnar frameworks (Xu et al., 2021). MOFs have also displayed immense potential and implementations like heavy metal ions removal from aqueous solution. Furthermore, the metal nodes, organic linkers, and the functional groups embedded on MOFs surface can all chelate heavy metal ions to initiate stable complex (Xu et al., 2021). Based on these advantages, MOFs have gained a lot of attention and been viewed as one of the greatest hotspot as a high-performance adsorbent towards diverse heavy metal ions including lead(II) (Ghaedi et al., 2018).

The capacity of MOFs to maintain their long-ranged ordered structure in certain chemical conditions is referred to as chemical stability while the improved strength of the coordination bonds between inorganic clusters and coordination groups is the most basic way to prevent the MOF degradation in water vapour or liquid water, where it is a sequence of substitution processes in which metal- coordinated linkers are replaced by water or hydroxide (Yuan et al., 2018). In water stability context, the comparison of typical physicochemical features between post-exposure and pristine samples is principally the essential criteria for determining whether a MOF structure stays intact in the water stability test. The powder X-ray diffraction (PXRD) pattern and gas adsorption capability, as a rule of thumb, may indicate if the MOF loses its crystallinity or structural porosity (Liu et al., 2020). Table 2.4 showed the different kinds of MOFs and its crystallinity degradation stability).

Table 2.4: The Stability of MOFs in Aqueous Solutions or Humid Environments

MOF	Crystallinity	Linker	Hydrophilic and Hydrophobic	References
MOF-5(Zn)	complete degradation in all conditions	1,4-benzene-dicarboxylate (BDC)	Hydrophilic	(Guan et al., 2019)
ZIF-8 (Zn)	complete degradation in all conditions	2-methylimidazole (MIM)	Hydrophobic	(Guan et al., 2019)
PCN- 602(Ni)	well-retained in all conditions	tetra(4-phosphonophenyl)porphyrin (TPPP)	Hydrophilic	(Lv et al., 2017)
MIL-101(C) hydrophilic	well-retained in all conditions	1,4-benzene-dicarboxylate (BDC)	Hydrophilic	(Leus et al., 2016)
HP-UiO-66(Zr)	well-retained in all conditions	1,4-benzene-dicarboxylate (BDC)	Hydrophilic	(Cai and Jiang, 2017)
HKUST-1(Cu)	partial degradation in all conditions	benzene-1,3,5-tricarboxylic acid (BTC)	Hydrophilic	(Zhang et al., 2017)

2.7.1 Zeolitic imidazolate framework-8 (ZIF-8)

Zeolite imidazolate frameworks (ZIFs) have emerged as a distinct and fascinating family of MOFs among the numerous robust MOFs discovered so far, exhibiting the characteristics of both zeolites and MOFs (Nagarjun and Dhakshinamoorthy, 2019). Generally, ZIFs are a type of MOFs with a zeolite skeleton framework that are made by reacting Zn or Co with imidazole or imidazole derivatives as organic ligands in a solvent (Dai et al., 2021). In a simpler word, ZIFs are porous in nature and are formed by the coordination of N-atoms in imidazolate anions with metal ions such as Zn^{2+} or Co^{2+} . ZIFs have a structure comparable to zeolites, which are made up of four-connected webs of tetrahedral components (Makhetha and Moutloali, 2020). ZIFs have had a positively influence on membrane features such as hydrophilicity and surface roughness, resulting in

increased water flux, solute rejection, and antifouling (Kim et al., 2019). ZIFs have been included and used in most membrane separation technologies such as reverse osmosis, nanofiltration, ultrafiltration, and microfiltration due to their chemical, thermal, and hydrostability (Makhetha and Moutloali, 2020).

Besides, a typical MOF material is ZIF-8, which is made up of metal atoms Zn and 2- methylimidazole according to (Dai et al., 2021). ZIF-8 is one of the most representative ZIF-based MOFs, in which ZnN₄ tetrahedra are consists of divalent zinc cations connected across four imidazolate-based anion linkers, resulting in cages measuring 11.6 Å in diameter and reachable through narrow six ring pores (3.4 Å) with sodalite zeolitic network topology (Nagarjun and Dhakshinamoorthy, 2019). Zeolite imidazole framework-8 (ZIF-8) has been used a lot to make high-performance separation membranes because of its microporous framework structure and 6-membered pore aperture of 0.34 nm. This is ideal for separating water molecules from their solutes (Zhang et al., 2021).

Because of its unique characteristics, ZIF-8 has a high adsorption capacity and an excellent host ability for photocatalytic materials, making it a high-profile material in wastewater treatment (Dai et al., 2021). ZIF-8 may also maintain its crystallinity and porosity after being dissolved in a variety of solutions, including water and organic solvents (Troyano et al., 2019). Figure 2.9 showed the structure of ZIF-8 and topology.

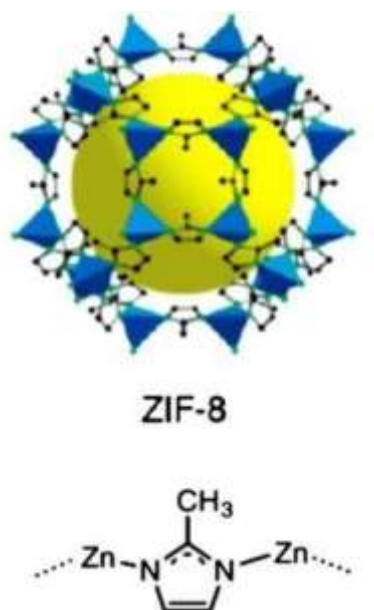


Figure 2.9: ZIF-8 topology and crystal structure (Zhang et al., 2020)

The synthesis techniques of ZIF-8 are more diverse and uncomplicated than those of other MOF compounds and has a better chemical and hydrothermal stability, which is aided by its robust link structure. Consider, for instance, its thermal stability: ZIF-8 can sustain structural integrity at temperatures over 500 °C (Dai et al., 2021). ZIF-8 materials have become widely utilized in a variety of forms, such as powders, colloid, membranes, and thin films, and have been used in a variety of vital sectors (Schelling et al., 2020). ZIF-8's pore sizes and architectures are relatively tailorable, which makes it useful for customization. In addition, the development of mesoporous and multistage porous ZIF-8 broadens the application range of conventional microporous ZIF-8 significantly. On the surface of ZIF-8, there are many active spots and facial charge separation. They also have poor recyclability since it is difficult to extract them from water once the contaminant has been removed (Dai et al., 2021).

Through the controlled integration of ZIF-8 and functional materials, emergent multifunctional composites/hybrids may be produced. These composites or hybrids have greater characteristics than separate components due to the combined behaviour of each functional unit, and have received a great deal of interest (Li et al., 2018). Until now, active species such as metals, oxides, polyoxometalates (POMs), fibres, polymers, graphene, and carbon nanotubes (CNTs) have been effectively synthesised in ZIF-8 modified combinations as shown in Figure 2.10.

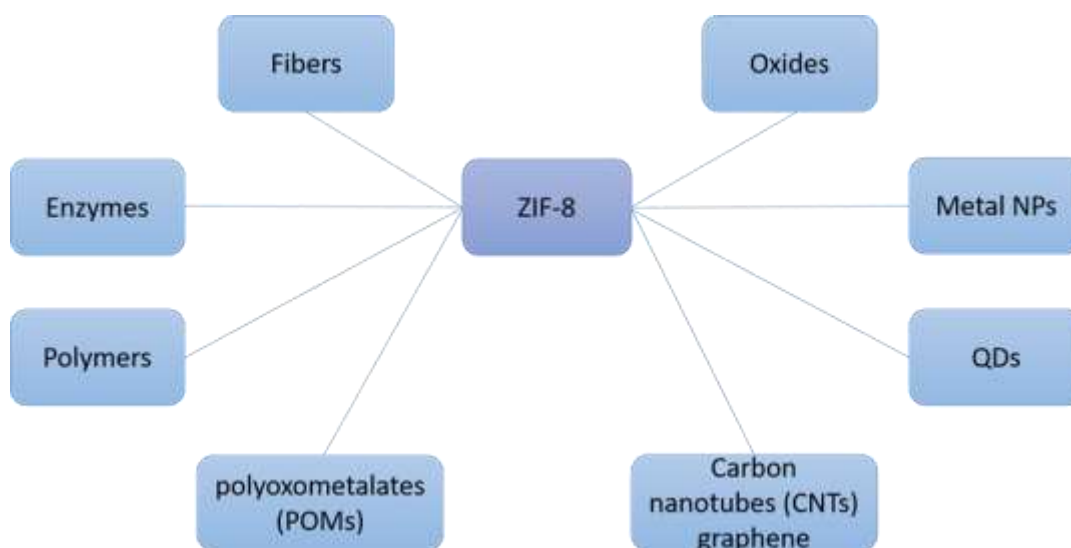


Figure 2.10: The modification of ZIF-8 with functional materials species (Dai et al., 2021)

2.7.2 Limitation of ZIF-8

The introduction of ZIFs into water during wastewater treatment may lead to environmental contamination. ZIFs exhibit stability issues, making their natural entry into water possible. The surface of ZIFs, formed through the chemical bonding of zinc ions, cobalt ions, and imidazole, is relatively hydrophobic and not soluble in water. Furthermore, recent studies have revealed that immersing ZIFs in water results in the loss of their central metal ions, contributing to potential secondary pollution (Pouramini et al., 2023). To ensure

the ZIFs from potential structural deterioration resulting from an attack on their metal coordination bonds, appropriate consideration is a must for the enhancement of their stability. The utilization of ZIF powder in processes may give rise to complications such as pipeline blockages and the inadvertent loss of adsorbents during treatment. Significantly, the expeditious and efficient separation of spent ZIFs from treatment chambers is imperative. Current researchers are actively investigating diverse methodologies aimed at optimizing the interaction between contaminants and ZIFs, thereby ensuring both the secure and efficient reutilization of ZIFs (Ying et al., 2019; Qiu and He, 2019). In brief, nanomaterials incorporating ZIF-8 may exhibit the capacity to mitigate adsorbent aggregation and thus, facilitating a more efficient separation of the adsorbent from water. ZIF-8 composites demonstrate enhanced adsorption capacity and recyclability compared to their individual constituents when employed in the elimination of water contaminants (Dong et al., 2019; Pouramini et al., 2023). Table 2.5 shows the comparison of ZIF-8 composites and their synthesis method from the published literature.

Table 2.5: The comparison of ZIF-8 composites and their synthesis method

Composites	Synthesis Method	Reference
ZIF-8@PTA/Au	Hydrothermal	(Akbari Beni et al., 2020)
Fe ₃ O ₄ @ZIF-8	Carbonization	(Al-Hazmi et al., 2023)
ZIF-8/PAN	Solvothermal	(Li et al., 2022)
CS-ZIF-8	In-situ synthesis	(Wang et al., 2022)
ZIF@GO	Solvothermal	(Li and Xu, 2021)
nFe@ZIF-8	Conventional liquid-phase reduction	(Zhou et al., 2020)

2.8 Nanomaterials

Over the past two decades, numerous nanomaterials have been studied extensively for their potential to provide new answers or improve current solutions to many of the world's most major environmental issues, ranging from water pollution to air pollution (Long et al., 2021). Nanotechnology advancements have made it possible to create nanoparticles with the desired shape form, size, and aggregation. It is critical not only to develop new nanoparticles that are sustainable, non-toxic, and biocompatible, but simply to use renewable precursors in the synthesis process (Rajan et al., 2018).

2.8.1 Carbon dots (CDs)

Carbon dots (CDs), also known as carbon quantum dots, characterised with a size below 10 nanometres, plus defined as non-toxic, very stable, high water and aqueous solubility, photochemical stability (resistance to photobleaching) (Li et al., 2021), biologically compatible, and simply to synthesise and functionalize materials (Ng et al., 2021). CDs have recently gained a lot of interest due to their unique physical chemistry features, ultra-small size, high biocompatibility, and plentiful and affordable precursor (Long et al., 2021). In general, CDs are amorphous to nanocrystalline quasi-spherical nanoparticles that usually include sp^2/sp^3 carbon, oxygen/nitrogen based groups, and post-modified chemical groups (Sun and Lei, 2017). Conforming to Devi et al. (2019), CDs can be easily improved their selectivity by providing possible binding sites (Li et al., 2021) against new targets due to their easy surface modification employing a broad range of intrinsic reactive and functional groups (e.g., carboxyl, epoxy, and hydroxyl).

As an alternative to conventional adsorbent materials, carbon-based nanomaterials such as CDs and graphene have been produced. When compared to graphene materials, using CDs as adsorbents has a number of advantages. Due to their compact size and huge specific

surface area, CDs can provide a large number of surface adsorption sites. Furthermore, CDs may be readily synthesised using a simple method for producing a large number of CDs. Furthermore, CDs can be easily synthesised utilising a simple process that uses ubiquitous and low-cost raw items and does not require the use of complicated apparatus (Long et al., 2021). Additionally, considering the generated CDs-based material already contains a large number of hydrophilic functional groups that may be responsible for CDs' ability to absorb pollutants, no further modification procedure is necessary to give the CDs hydrophilic characteristics and reactivity (Long et al., 2021; Mehta et al., 2019).

According to a study by Sabet and Mahdavi (2019), nitrogen-doped carbon dots (CDs) were used to adsorb Cd^{2+} and Pb^{2+} ions from wastewater. The CDs were discovered to have a large specific surface area, which can aid in the adsorption of heavy metal ions from water. At the same time, negatively charged nitrogen elements and oxygenated-functional groups on CD surfaces can operate as active sites for metal ion adsorption. In terms of metal ions adsorption, due to a mass of negatively charged oxygen-containing groups on the surfaces of CDs, it has been claimed that electrostatic attraction and $n-\pi$ stacking interactions may perform a key role in the molecular interaction between metal ions and CDs-based composite absorbents (Long et al., 2021). In short, CDs' enormous specific surface area, extensive surface functions, and rich -domains allow them to interact well with organic molecules and metal ions, potentially leading to applications in wastewater treatment (Feng et al., 2021).

2.8.2 Carbon dots (CDs) synthesis

Furthermore, owing to well-established synthesis processes (such as pyrolysis, hydrothermal synthesis, microwave synthesis, and so on), they are also favourable for commercial scale-up. A considerable amount of literature on CDs synthesis routes has been

stated by Ng et al. (2021). CDs are mostly synthesised in one of two ways: top-down or bottom-up. Breaking down bigger carbon structures into CDs is referred to as top-down approaches, whilst generating small CDs from molecular precursors is referred to as bottom-up methods. In top-down processes, nanoparticles are created via arc discharge, laser ablation, chemical, or electrochemical oxidation and a range of carbon materials, including nanodiamonds, graphite, carbon nanotubes, carbon soot, and activated carbon have been produced through this approach (Sun and Lei, 2017). In contrast, CDs that are made in bottom-up approaches by combining molecular precursors (such as citrate, polysaccharides, biomaterials, sucrose, ascorbic acid, polymer-silica nanocomposite, glucose) under a variety of reaction conditions, such as microwave-assisted synthesis, supported synthetic conditions hydrothermal methods, pyrolysis, or carbonization (Wang et al., 2017; Sun and Lei, 2017; Li et al., 2021).

Because of its solvent-free procedure, simplicity of operation, fast reaction time, scalability, and utilisation of very numerous and economical precursors, the hydrothermal and microwave processes are the most commonly employed in environmental applications of CDs (Long et al., 2021). Most notably, under mild reaction conditions, one-pot synthesis for doping modification is practicable. Most carbon precursors, including bio-waste and chemical sources, are acceptable for these procedures. The production of CDs is generally indicated by the presence of yellow, orange, or brownish solutions created utilising various sources and procedures. After synthesis, high-speed centrifugation is used to remove large, undissolved particles, followed by membrane filtration or dialysis to eliminate any remaining contaminants. CDs are kept in distilled water, however they may be dried into solid particles for many uses (Ng et al., 2021).

However, bottom-up techniques have their own drawbacks, including as higher energy consumption at a bigger scale, the need for acidic chemical precursors, and specific and costly equipment (Rajan et al., 2018). The majority of synthesis processes need complex equipment, toxic chemical reagents, catalysts, long reaction time, non-environmental chemicals, or severe experimental conditions, all of which lead to high production costs (Feng et al., 2021). To overcome this problem, biomass emerges as a viable alternative precursor that provides a high-quality, long-term source of energy (Rajan et al., 2018). While exploring environmentally friendly methods to synthesize CDs, it is also important to investigate ways to stabilize them, so that carbon dots can fully realise their potential in wastewater treatment applications. Fabrication of CD-based nanocomposite materials can be accomplished by incorporating CDs into compatible solid matrices via intermolecular interactions or covalent bonding (Feng et al., 2021).

By integrating CDs into compatible solid matrices, CDs' unique properties can endow solid matrices with additional properties such as increased mechanical strength, superior fluorescence performance, ionic conductivity, bioactivity, self-healing, and stimuli-responsiveness while help to manage the nanocomposite macro-morphology. Simultaneously, this technique also provides additional benefits for the CDs, such as greater mobility, self-supporting ability, quick electron or heat conductivity, and improved chemical stability (Ma et al., 2018; Wu et al., 2020; Feng et al., 2021).

The conventional CD synthesis processes need costly precursors, hazardous chemicals, solvents, the use of oxidising agents, and a large quantity of energy, either in the form of higher temperatures or electrical energy, all of which add to the environmental load. Continuous advances in CD applications have led to the development of environmentally sustainable, efficient, and low-cost green synthesis of CDs using renewable biomass or

biowastes as precursors using modified bottom-up approaches under comparatively milder reaction conditions based on green chemistry principles (Agarwal and Bhatia, 2021). The different renewable biomass had been used vastly in different kind of applications as literature in Table 2.6.

Table 2.6: The carbon dots synthesis from biomass source and their applications

Biomass	Application	Method	References
Rice Husk	Dye Removal	Hydrothermal	(Heng et al., 2021)
Sago Waste	Probe for metal ion sensing	Pyrolysis	(Tan et al., 2014)
Durian peel waste	Composite electrode	Pyrolysis	(Praneerad et al., 2019)
Sago Waste	Drug delivery and bioimaging	Pyrolysis	(Abdul Manaf et al., 2017)
Tulsi leaves (<i>Ocimum sanctum</i>)	Pb ²⁺ ions and live cell imaging	Solvothermal	(Kumar et al., 2017)
Tapioca	Adsorption of heavy metal ions (lead)	Hydrothermal	(Pudza et al., 2020)

2.8.3 Biomass waste: sago *hampas*

Biomass materials are ubiquitous in our environments, and their low cost, accessibility, environmental friendliness, carbon richness and recyclable qualities make them great candidates for carbon materials supplies (Yang et al., 2019; Ma et al., 2017). Carbons derived from biomass materials are inherently porous or hierarchically organized, making electrolyte penetration easier and reducing ion diffusion distance (Tang et al., 2017). Malaysia is currently the world's third largest sago producer, behind Indonesia and Papua New Guinea, where sago is predominantly cultivated for sago starch. Sarawak, which is one of the world's top sago exporters, exports around 25,000–40,000 tonnes of sago products

annually to Peninsular Malaysia, Japan, Taiwan, and Singapore, accounts for more than 90.0 percent of all sago-planting areas in Malaysia (Amin et al., 2019).

Currently, Sarawak is among the world's leading producers of sago starch, exporting more than 40,000 tons every year to different Asian countries. Based on the data by Department of Agriculture Sarawak (DAS) (Figure 2.11), it was reported that the value of exports in 2017 increased slightly, indicating that sago starch exports would continue to rise in the future (Amin et al., 2019).

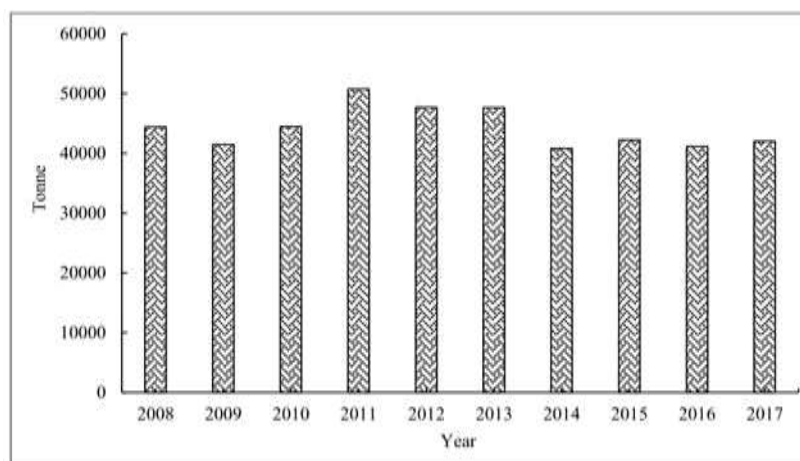


Figure 2.11: Malaysian sago starch export data from 2008 to 2017 (Amin et al., 2019)

When demand rises, so does sago production, which adds to the large quantity of waste produced. As a result, the sago sector is grappling with waste disposal and management issues. Fundamentally, sago wastes comprise starch, hemicellulose, cellulose, and lignin; where it can be valorised into a precursor of carbon products. In the past study by Heng et al. (2021), the polysulfone (PSf) membrane was modified by incorporating rice husk biomass-derived carbon dots with silica composites to improve the permeability and dye rejection. In another study by Tan et al. (2014), has proven the conversion of sago waste into highly fluorescing carbon dots using a simple thermal pyrolysis approach that may not

require any surface passivation. As by Abdul Manaf et al. (2017), they proposed a single-step pyrolysis carbon nanospheres from sago bark material for cancer cell imaging applications in favour of giving encouragement for environmental sustainability. These previous literature as summarized above provide insights on the synthesis of carbon dots from biomass specifically sago waste and confirm the potential use of carbon dots in different types of application. To sum up, the sago waste is possible to be implemented as alternative carbon precursor that is sustainable, environmentally favourable, widely accessible, and harmless. Nevertheless, in this study the application of carbon dots in membrane system to remove heavy metals become a bridge with the others previous carbon dots application studies; (biological cell imaging (Ang et al., 2020); Composite electrode (Praneerad et al., 2019); Pb²⁺ ions and live cell imaging (Kumar et al., 2017); Dye removal (Heng et al., 2021)). Despite there are still presented study (Pudza et al., 2020) that employed the carbon dots in the lead heavy metal adsorption, the biomass used was tapioca waste where it is still different with the composition of lignocellulosic in sago waste. Until now, sago industrial waste has also been utilized as a carbon source for the creation of carbon dots nanomaterials (Kang et al., 2020). Thus, the exploration of carbon dots derived from sago waste for lead removal is a promising advancement in addition to solve the sago waste management issue.

As explained by Rajan et al. (2019), solid waste wastes from the sago industry is known as sago hampas. In Sarawak, it is estimated that 260 tonnes of sago hampas are produced each year and disposed of into a nearby river. The high organic content in sago hampas, may produce an increase in river water biochemical oxygen demand (BOD) and chemical oxygen demand (COD) (Ngaini et al., 2021).

Sago hampas known as sago pith residue, a starchy lignocellulosic by-product and it is cheap fibrous waste left over from the starch extraction process, specifically as the result of crushing and sieving as shown in Figure 2.5. Sago pith residue, a starchy lignocellulosic by-product, is another name for it (Amin et al., 2019). Sago hampas are composed approximately 37.0-49.7% of starch, 20.2-40.0% of cellulose, 7.9-14.5% of hemicellulose, and 3.3-7.5% of lignin, all of which are extensively used in biosorbents and other applications (Rajan et al., 2019; Amin et al., 2019).

This lignocellulose residue was recommended as a competent and promising bio-sorbent for heavy metal adsorption in its raw form (Droepenu et al., 2020). The extraction of sago hampas was gone through journey of flow process from sago logs until sieving process to obtain the *hampas* as Figure 2.12.

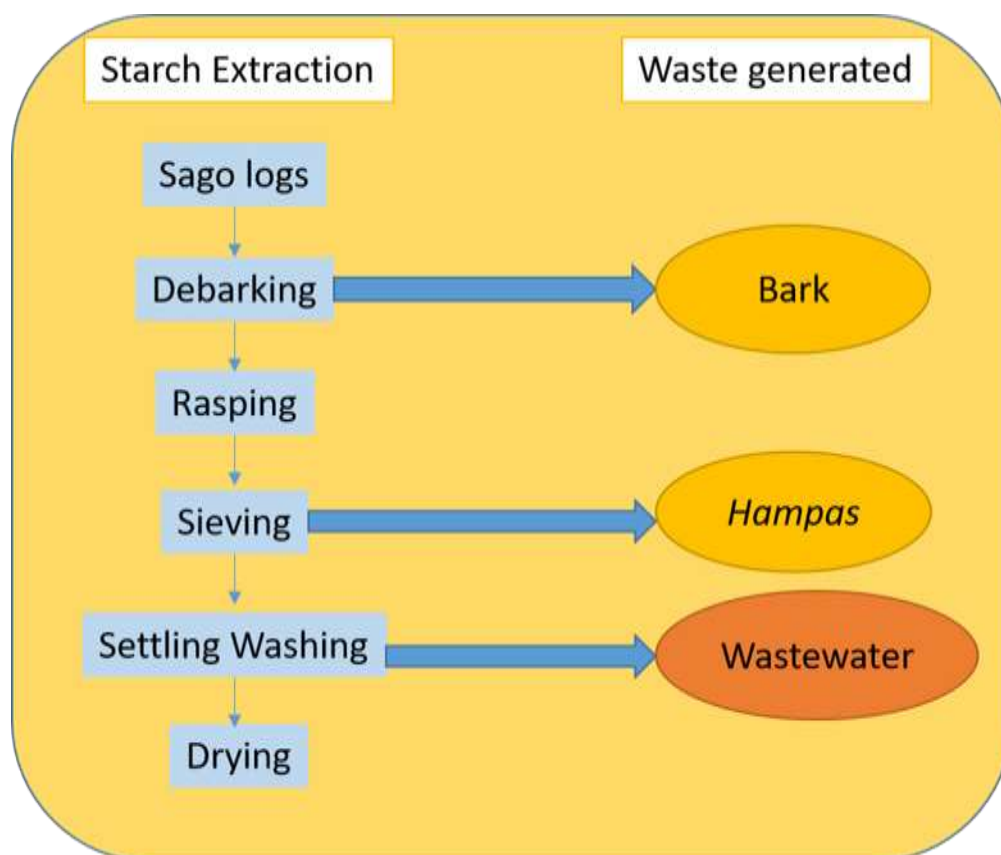


Figure 2.12: The extraction of sago starch is depicted in this flow diagram (Amin et al.,

2019)

Lignocellulosic biomass is characterized by natural porousness, a hierarchical structure, and a high surface area (Tang et al., 2017). The porous structure is advantageous because it allows for ion movement; it may also be easily mixed with other materials to create a hybrid material with improved electrochemical characteristics (Xiao et al., 2017). Lignocellulosic is also known as a carbon-rich material with heteroatom-doping properties, which makes it appealing for application as a carbon-replacement material (Tang et al., 2017).

2.9 Cross-flow filtration system

Conventionally, membrane designs may be made to either retain macromolecules through ultrafiltration or particles through microfiltration. In order to prevent the membrane surface from being fouled, membrane operations can either run in cross flow (tangential flow) filtration (CFF) mode or in a normal flow (dead end) filtration (NFF) mode, which is frequently used to remove trace particles (Fernandez-Cerezo et al., 2019). In the same vein, CFF, as contrasted to dead-end filtration, is fundamentally different because the solution mixture typically moves tangentially over the membrane's surface instead of passing straight into it (Downing et al., 2023). Dead-end mode is best suited for feed with low concentrations due to the rapid membrane fouling that occurs at high concentrations. This procedure uses more energy than cross-flow but less as a flocculation or vacuum filtering process (Leam et al., 2019). Figure 2.13 showed the diagram of cross-flow and dead-end filtration.

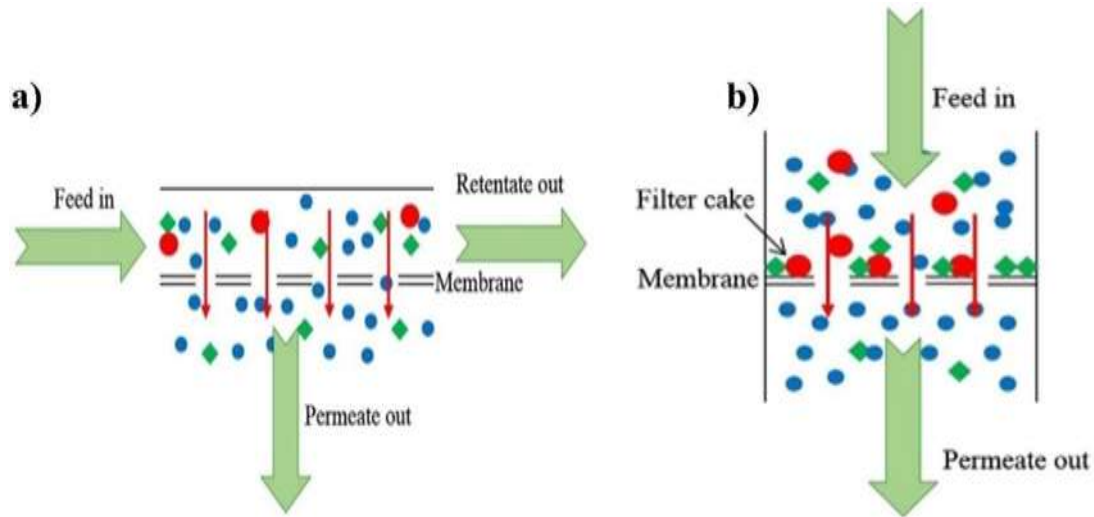


Figure 2.13: a) Cross-flow and b) dead-end membrane filtration diagrams (Meshksar et al.,2020)

Until the advent of the CFF system technique, downstream procedures for fluid filtrations took much longer and required more manpower. With the advent of the CFF system in the early 1990s, operations have become so simple in terms of time and personnel consumption, with an excellent yield in terms of product production (Sravan Kumar and Kumar, 2022).

In addition, the ceramic membranes are frequently used in cross-flow filtration (Gu et al., 2021). As a crucial parameter in the cross-flow mode, A rise in transmembrane pressure (TMP) also results in an increase in filtration flux because of the high turbulence brought on by increased cross-flow velocities and shear stress, which prevents pollutants from depositing on membrane surfaces. Though, as TMP continues to rise, cake layer formation causes a permeance drop. Thus, by only increasing TMP above a particular threshold value may permeance be increased (Leam et al., 2019). Crossflow filtering can minimise foulant deposition and demonstrate self-cleaning abilities by displaying tangential shear. High shear rates close to the membrane surface help remove foulant and prevent the development of the cake layer from a hydrodynamic standpoint (Wang et al., 2021). Figure

2.14 depicts the CFF system's operating flow pattern in an accessible, methodical, and comprehensible manner.

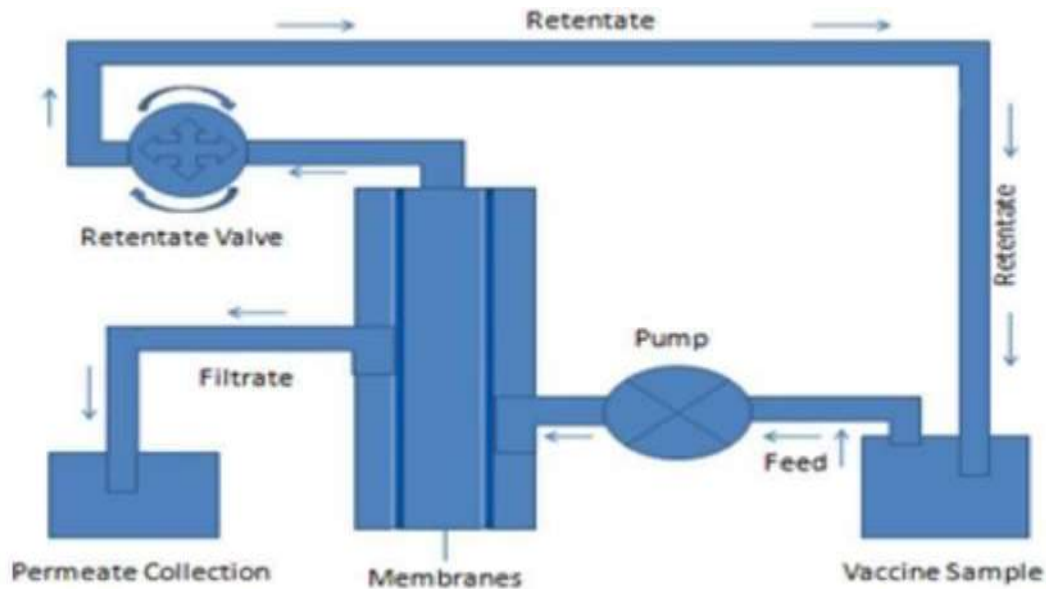


Figure 2.14: CFF system operation route (Wang et al., 2021)

In other cases, the NFF inhibits high shear stress from occurring but shortly causes severe concentration polarisation, membrane fouling, and poor fluxes through the membrane (Tan and Franzreb, 2020). In CFF, the transmembrane pressure propels the fluid through the membrane, whilst cross-flow velocity generates a force that pushes molecules away from the membrane surface, increasing back diffusion and minimising the flux drop triggered by membrane fouling (Madsen et al., 2022). In a nutshell, both flow geometries offer benefits and drawbacks. For example, dead-end separation membranes are less costly and easier to construct than crossflow filtering. A batch-type procedure in which the feed solution is gradually injected into the membrane medium is also known as dead-end membrane. As a result, it is mostly employed in labs for separation. The drawbacks of the primary dead-end membrane include concentration polarisation and membrane fouling. Cross-flow filtering

systems are more costly and time-consuming, but they are less susceptible to fouling due to sweeping actions and high passing flow shear velocities (Meshksar et al., 2020).

As mentioned in the prior study the comparison between CFF and NFF had been made. Water flux was higher in CFF than in NFF. This is owing to the effective area has grown larger. Therefore, the CFF resistance is lower compared to NFF resistance due to the larger flux (Anwar and Arthanareeswaran, 2019). This is consistent to the study by Gu et al. (2021). The pure water flux and antifouling performance of the perpendicular patterned flow ceramic membranes are significantly improved compared to those of angle, parallel (like NFF) patterned, and non-patterned membranes. The largest stable permeate flux is seen via the perpendicular flow due to their maximum fluid velocity and surface stress benefits (Gu et al., 2021). These explanations reflect those of Li et al. (2019) who studied on the preparation of stable graphene oxide (GO) dispersions via cross-flow membrane filtration. Through the study, the process condition such as tangential velocity has been comprehensively studied by concluding the high tangential velocity show outstanding filtering performance for the determined GO dispersion (Li et al., 2019). This study supports evidence from other studies which stated that the larger particles (more than 90nm of the nominal pore size of the top layer) would congregate on membrane surfaces to form a cake layer under the CFF and cross- flow velocity of 4 cm/s across the studied membrane surface. Fortunately, by tangential flow the membrane fouling had been minimised (Ng et al., 2020).

CHAPTER 3

METHODOLOGY

The research was performed by dividing the methodology into three phases in order to fulfil the study's objectives.

3.1 Materials

Alumina oxide powder, NMP solvent, arlcel, polyethersulfone (PES), 0.06 mol ammonia solution, sago waste, 3-(aminopropyl) triethoxysilane (APTES), acetone, toluene, methanol, N,N-dimethylformamide (DMF), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 2-methylimidazole (mIm).

3.2 Preparation of carbon dots-ZIF-8 membrane

3.2.1 Preparation of carbon dots from sago *hampas*

The carbon dots was prepared according to the reported synthesis procedure (Zhang et al., 2016) with slight modification as shown in Fig 3.0. The carbon dots were synthesized using a hydrothermal process using sago waste as the carbon source and ammonia as the nitrogen supply, 4.2 g of sago waste was dissolved in 40 mL of deionized water and then combined with 0.06 mol (4.5 mL) of ammonia solution under vigorous stirring. The solution was transferred to 100 mL Teflon-lined stainless-steel autoclaves and heated for 8 hours at 160°C, and 200°C, respectively. After then, the reactor was naturally cooled to normal temperature. The crude product was centrifuged at 15000 rpm for 30 min to separate the supernatant with the residues, and then filtered with 0.45 μm filter membranes to remove large particles (Singh and Singh, 2020).

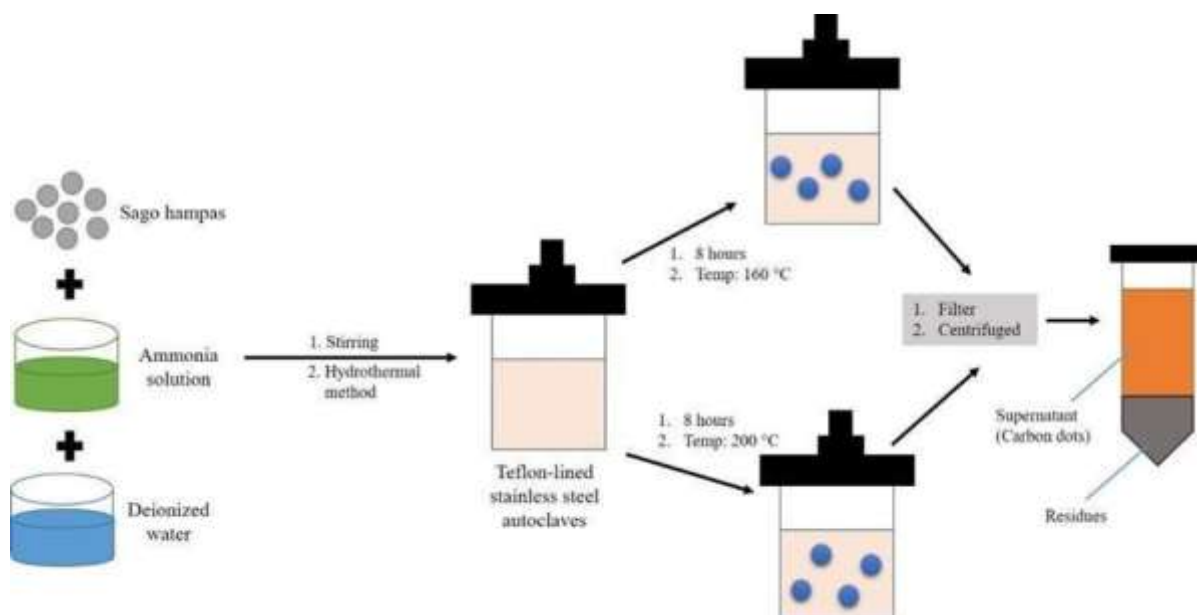


Figure 3.1: The preparation of CDs through the hydrothermal method

3.2.2 Modification of alumina hollow fibre membrane using 3-(aminopropyl)triethoxysilane (APTES)

The APTES modification on the alumina hollow fibre membrane support was carried out in accordance with the prior procedure (Awang Chee et al., 2021). First, the alumina hollow fibre membrane was sonicated for 5 minutes in deionized water, acetone, and methanol. The cleaned alumina hollow fibre membranes were silanized for 2 hours in a 2% APTES solution in toluene. Next, the modified membrane was rinsed with ethanol and dried after the process. Before proceeding to the solvothermal of ZIF-8, the solvent on the membrane's surface was removed via heating the membranes in the oven at 60 °C for 30 minutes period of time.

3.2.3 In-situ solvothermal preparation of carbon dots-ZIF-8 membrane

The solvothermal approach, which involves introducing the right organic solvents, temperature, and reaction time, is one of the most popular and effective procedures for crystalline materials. ZIF-8 was originally obtained using a solvothermal technique

including N, N-dimethylformamide (DMF), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 2-methylimidazole (mIm) at 140 °C for 24 hours as per literature (Jin and Shang, 2021) as shown in Fig 3.1. The carbon dots-ZIF-8 membrane was prepared by following the method as described in the synthesis procedure (Guo et al., 2020). Briefly, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.210 g, 0.803 mmol) and 2-mIm (0.060 g, 0.731 mmol) were dissolved in 18 mL of DMF, then 10 mg of as-synthesized CDs were added into the solution. The ZIF-8 precursors, and carbon dots was reacted at 140 °C for 24 hours after being agitated for 30 minutes in DMF (Guo et al., 2020). The synthesis solution was placed at room temperature in a poly(tetrafluoroethylene)(PTFE, Teflon) lined flasks (50 mL) containing the modified alumina hollow fibres. To prevent the synthesis solution from entering the lumens prior to the synthesis process, both ends of the alumina hollow fibre were covered with PTFE (Guo et al., 2020; Mahpoz et al., 2019). After the solvothermal procedure has completed, the carbon dots ZIF-8 membranes were cooled to room temperature before being washed multiple times with DMF and DI-water (Guo et al., 2020), to remove loosen ZIF-8 powder on the membranes' surface, and subsequently dried for 24 hours at room temperature (Mahpoz et al., 2019).

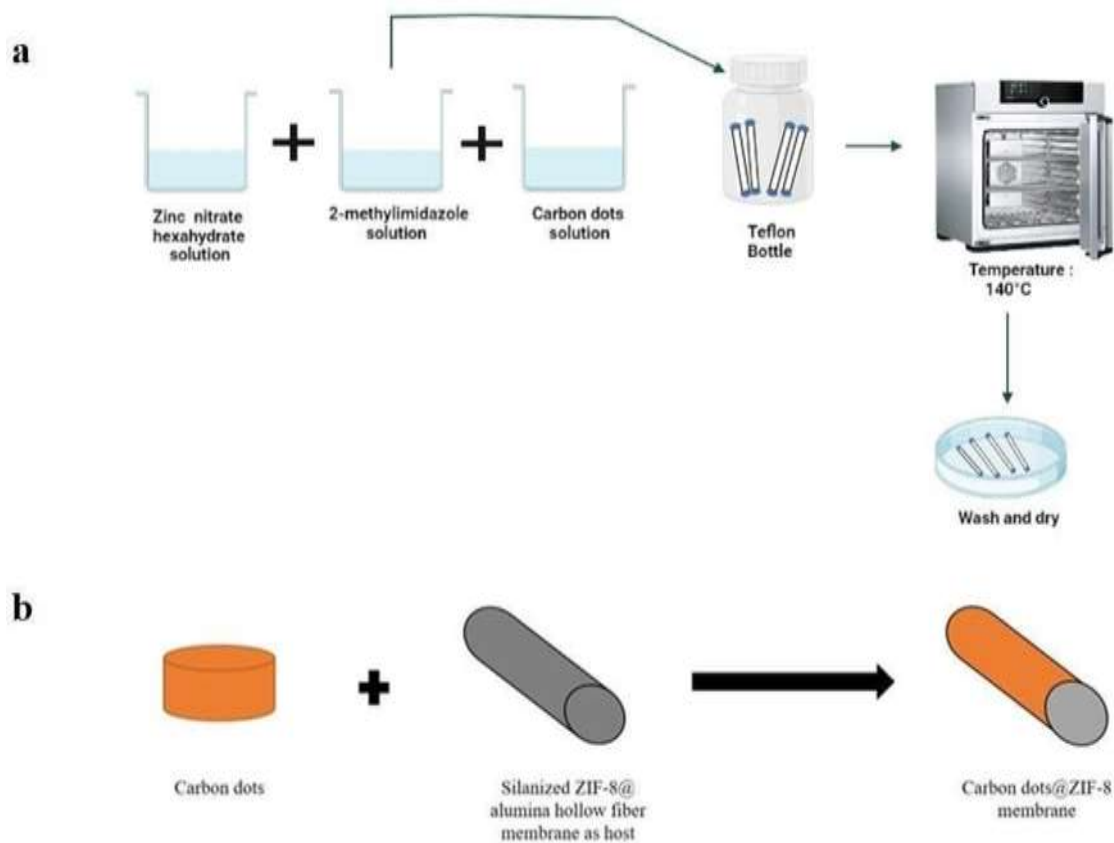


Figure 3.2: (a) In-situ solvothermal preparation of carbon dots-ZIF-8 membrane (b) the illustration of CDs@ZIF-8 membrane modification.

3.3 Membrane characterization

3.3.1 Scanning electron microscopy scanning (SEM) / Electron dispersive X-ray (EDX) spectroscopy

About 0.5 cm of the CDs@ZIF-8 membranes were attached onto the 1 cm × 1 cm platinum plate holder. The surface and cross-section of the membranes was analysed by using a scanning electron microscope (SEM) (JOEL JSM-IT500HR), coupled with energy dispersive X-ray (EDX) spectrometer. The sample was coated with platinum under vacuum condition for about 3 min at 20 mA to avoid surface charging during analysis. The coating not only improves the clarity of the analysed images, but it also lowers thermal damage to the sample caused by charge build-up (Alqaheem and Alomair, 2020).

3.3.2 Ultraviolet-visible (UV-vis) analysis

The optical characterization of the CDs was carried out using UV-vis spectrophotometer (Cary 60 UV-Vis, Agilent) in the range of 200–800 nm.

3.3.3 Fourier transform infrared spectroscopy (FTIR) analysis

Functional group analysis of the material was performed using Fourier Transform Infrared Spectroscopy (FTIR), (Thermo Nicolet IS10) operating in transmittance mode ranging from 4000 to 500 cm^{-1} .

3.3.4 X-ray diffraction (XRD) analysis

The crystalline structure was determined using X-ray diffractometer D5000 with $\text{CuK}\alpha$ radiation with a wavelength of 0.15406 nm at 40 kV and 40 mA. The step speed of $2^\circ/\text{min}$, ranging from 5° to 40° was used to record the samples XRD patterns.

3.4 Performance study on the removal of lead(II) by carbon-dots-ZIF-8 membrane

3.4.1 Batch adsorption study

Batch adsorption studies had been implemented to study lead(II) adsorption by immersing 0.10 g of the membrane in 100mL of lead(II) ion solutions. Then, the Atomic absorption spectrometry (AAS) (Thermo Scientific – ICE 3500) was used to evaluate the residual lead levels in samples collected over time (Manjili et al., 2020). The membrane's adsorption capacity and percentage of lead(II) removal had been determined.

Equation 3.0, q_e , was used to determine the equilibrium quantity of lead(II) adsorbed, and Equation 3.1 was applied to determine the efficiency of lead(II) removal (percentage).

$$q_e = \frac{V(C_0 - C_e)}{m} \quad \text{Equation 3.0}$$

$$\text{Removal Efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad \text{Equation 3.1}$$

where C_0 (mg/L) represented the lead(II)'s initial concentration in an aqueous solution, while C_e (mg/L) indicated the equilibrium lead concentration, V (L) represented the volume of lead solution used, and m (g) represented the mass of adsorbent utilized, C_t indicates the lead concentration over time.

The adsorption mechanism was determined using conventional adsorption-equilibrium models, as shown in Table 3.1. The adsorption isotherms, which are Freundlich and Langmuir models, were to explain the material's adsorption rate concerning adsorbent mass per unit. In contrast, kinetic models, pseudo first order, and pseudo second order explained the adsorption rate of the removal.

Table 3.1: Adsorption isotherms and kinetics models

Isotherms Models	Linear Equations
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L}$
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$
Kinetics Models	Linear Equations
Pseudo First Order	$\log(q_e - q_t) = \log q_e + \frac{k_{1p} t}{2.303}$
Pseudo Second Order	$\frac{1}{q_t} = \frac{1}{K_{2p} q^2} + \frac{1}{q_e} t$

3.5 Filtration study

The filtration study had been carried out using the cross-flow filtration system as reported by Awang Chee et al. (2020) to determine the water flux and the percentage of lead(II) removal by carbon dots-ZIF-8 membrane, Fig 3.2. The water flux rig comprised a pump, a 4 L feed tank, and a filtration hollow fiber membrane module. A cooling system had been used to keep the feed solution temperature at 25 °C. The feed solution had been pumped into the shell side of the module to start the system. Then, the feed water passed through the lumen side of the hollow fibre membrane and exited through the opposite unsealed end of the fibres. Deionized water (conductivity 1000 $\mu\text{S cm}^{-1}$) was utilized as the feed solution for pure water flux. The system operated at room temperature, with a feed velocity of 3.0 m s^{-1} and a transmembrane pressure of 1 bar. The feed solution flowed continuously for 30 minutes before the permeate was collected for initial stabilization. Pure water permeation was measured using Equation 3.2 (Awang Chee et al., 2020).

$$J_w = \frac{V}{t \times A \times \Delta P} \quad \text{Equation 3.2}$$

whereas J_w ($\text{L/m}^2 \text{ h}^{-1} \text{ bar}^{-1}$) indicates pure water permeation/ the water flux, the volume of water permeated through the membrane during the time period t (h) is denoted by V (L), A is membrane total surface area (m^2), and P represents trans-membrane pressure (bar).

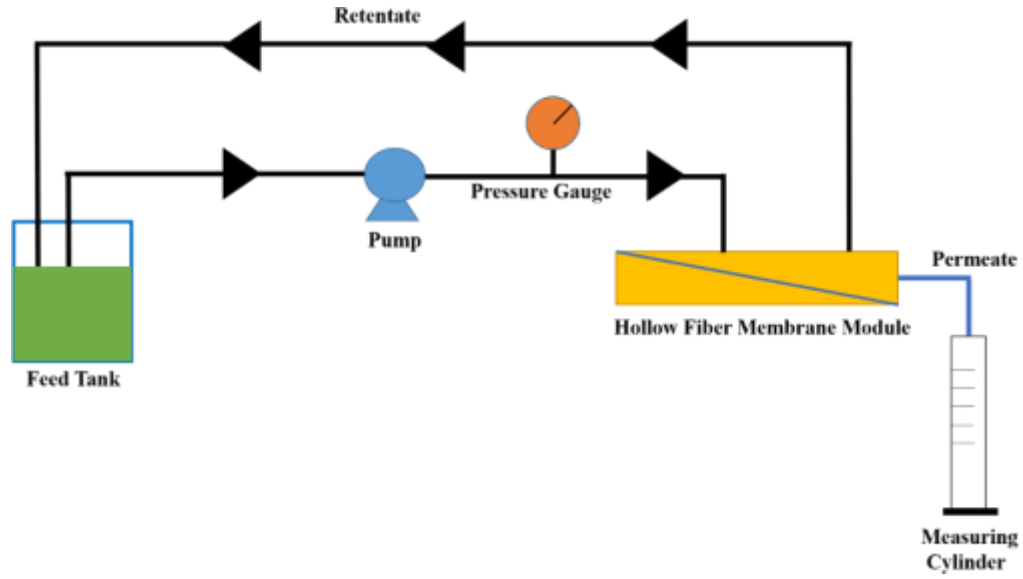


Figure 3.3: The schematic diagram of cross-flow filtration system

With respect to lead(II) removal determination, the lead(II) concentration on the performance of carbon dots ZIF-8 alumina hollow fibers was studied extensively. The lead(II) metal rejection (R%) were obtained from Equations 3.3 (Wu et al., 2021).

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad \text{Equation 3.3}$$

Where C_p is the concentration of the solute in the permeate and C_f is the initial concentration. Concentrations of permeate and feed solutions was measured using UV-vis spectrophotometer at a specific wavelength (DR5000, Hach Company, USA) (Wu et al., 2021). Blank wavelength scan with standard solutions for lead(II) was first performed prior to permeate sample analysis.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of carbon quantum dots

4.1.1 UV-Visible Spectroscopy

The synthesis temperatures of 160 °C and 200 °C were selected based on the study by Zhang et al. (2016), which investigated the effect of hydrothermal temperature on the structural and optical properties of nitrogen-doped carbon dots. Their findings demonstrated that CDs synthesized at these temperatures exhibited favourable size distribution, reduced aggregation, and enhanced photoluminescence characteristics. In particular, the 180 °C sample yielded the highest quantum yield, indicating an optimal balance between polymeric surface states and carbon core formation. Therefore, 160 °C and 200 °C were chosen in this study to explore the influence of moderate versus high thermal treatment on the adsorption properties of CDs.

The carbon dots (CDs) synthesized at 160 °C and 200 °C were examined under UV for their photoluminescence characteristic. The carbon dots 160 °C and 200 °C solutions turn to red luminescent under UV shortwave UV light as complemented with the result from (Ding et al., 2016). Both of them show blue fluorescence under the irradiation of a 365 nm ultraviolet lamp, but 200 °C CDs illustrated brighter than 160°C CDs (Fang and Zheng, 2021). The UV- vis spectrometry is an important tool for verifying the quality of CDs. By absorbing the energy produced, UV irradiation excites the electrons on CDs, causing them to be in an excited state. The fundamentals of CD fluorescence emission are provided by molecules of CDs with extended π -electron. The synthesized CDs shows a strong optical absorption in the UV region (230–340 nm) with a tail extending to the visible range (400

nm) as presented in Fig. 4.1d (Pudza et al., 2020). Absorption shoulders in the spectrum could be owing to the π - π^* transition of C=C bonds or n- π^* transition of C=O (Sahu et al., 2012). The fluorescence that CDs release is what gives them their distinctiveness. According to previous research, emission wavelength and intensity are dependent on excitation wavelength. This is caused by the varied surface chemistry and particle sizes at various emissive traps on the surface of CDs, which is connected to the synthesis process (Pudza et al., 2020; Wang and Hu, 2014). The 160 °C CDs and 200 °C CDs display distinctive absorption at 200 nm in their UV-Vis absorption spectra Fig. 4.1d, which is caused by the aromatic sp² domain's π transition (C=C) (Fang and Zheng, 2021). As illustrated from the figure, carbon dots 160 °C (red spectra) display their peak at 280 nm, while 200 °C (black spectra) at 285 nm and shoulder at 295 nm in the UV area. In contrast to the findings by Ding et al. (2016), the current study shows a single absorption peak at 255 nm and a shoulder at 282 nm in the UV region, which are attributed to the C=C bonds in aromatic rings. However, these bonds typically do not contribute to fluorescence emission.

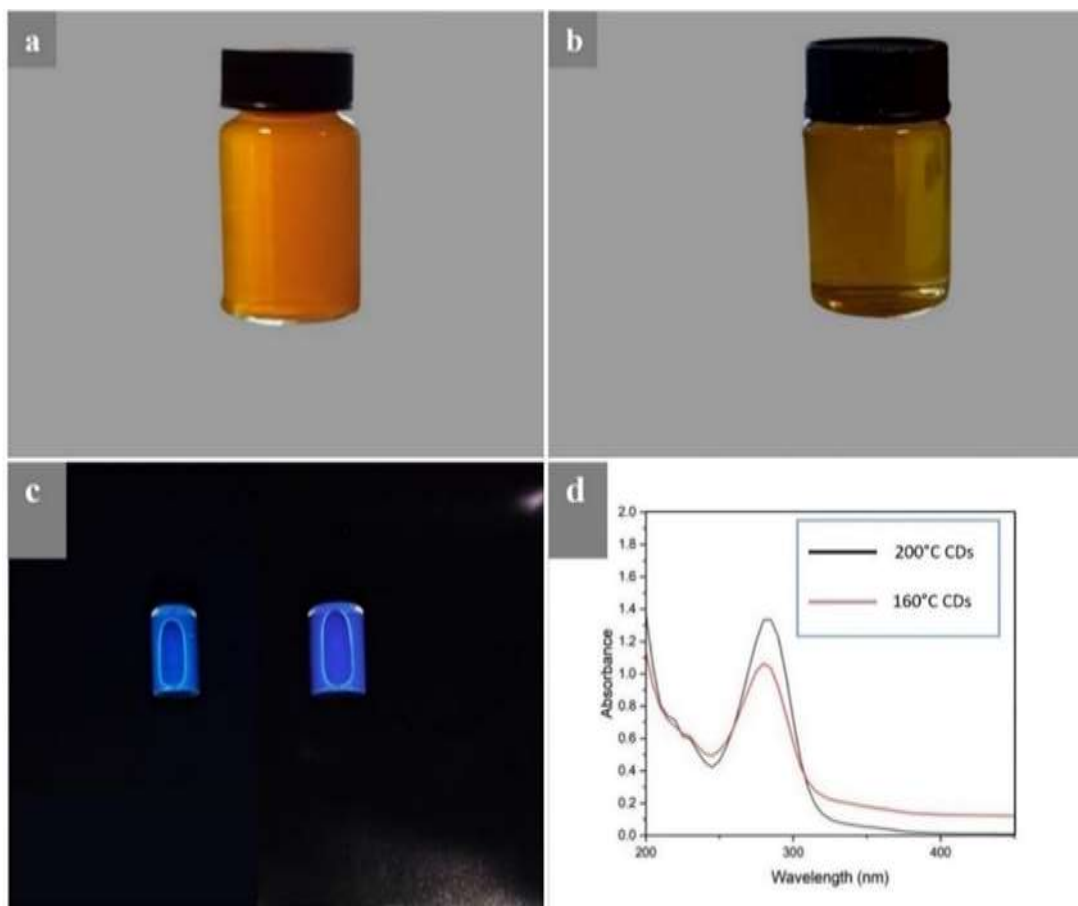


Figure 4.1: The carbon dots 200°C (a) under the daylight and (b) under the shortwave UV lamp which compared with the distilled water sample, carbon dots (left) and distilled water (right), (c) The carbon dots 200°C (left) and 160°C (right) under longwave UV lamp (d) Absorption curves (Abs) carbon dots 160°C (red spectra), 200°C (black spectra)

4.1.2 Fourier transformed infrared (FTIR)

Referring to Fig. 4.2, a broad and intense absorption band around 3285 cm^{-1} in the carbon dots synthesized at $160\text{ }^{\circ}\text{C}$ (red), and a similar band at 3289 cm^{-1} in the $200\text{ }^{\circ}\text{C}$ sample (blue), are characteristic of the O–H stretching vibration, which typically appears in this region and is commonly associated with alcohol or phenolic hydroxyl groups (Ma et al., 2019). The medium absorption at 1636 cm^{-1} was attributed to the generation of conjugated alkene C=C. Besides, the peaks at 1803 and 1025 cm^{-1} prove the existence of C-OH primary alcohol stretching and C-O-C groups in carbon dots (Ma et al., 2019). As for the carbon dots

treated at 200 °C (blue), it shows weak absorption at 2972 cm⁻¹, which corresponds to the C–H stretching vibrations. A small peak at 2190 cm⁻¹ (blue) and 2122 cm⁻¹ (red), attributed to the –C≡N stretching vibration, indicates the presence of amino-containing functional groups, which are essential for molecular conjugation (Kurdekar et al., 2016). (Kurdekar et al., 2016). The bending vibration of the C–O bond in the group of alcohol at 1406 cm⁻¹, suggests the presence of the carboxylic acid group. The existence of a carboxylic group in the sample's absorption spectra after treatment at 200 °C suggests that the cellulose and lignin residues have not fully devolatilized and carbonised (Tan et al., 2014). The medium C–N stretching can be illustrated by 1242 cm⁻¹ spectrum peak. As comparing to the pyrolysis process study, only at temperatures between 200 and 280 °C were lignin and cellulose in biomass discovered to initially devolatize and carbonise, followed by the release of carbon dioxide, acetic acid, and more moisture (Tan et al., 2014).

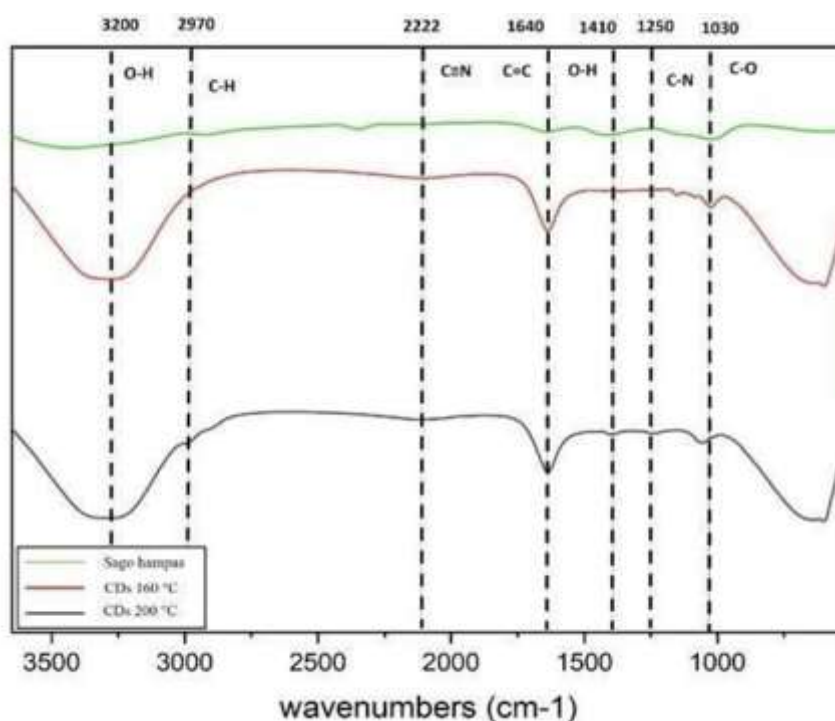


Figure 4.2: FTIR images of carbon dots 160°C(red), 200°C(black) and sago hampas (green) spectra CDs@ZIFmembrane (red)

4.1.3 Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX)

Fig. 4.3 displays SEM images of C-dots produced from sago *hampas* samples treated at 200 °C (Fig. 4.3a) and 160 °C (Fig. 4.3b), respectively. For the CDs synthesized at 200 °C, large clusters of irregularly shaped particles were observed. The size range of the particles was between 0.157 μm and 0.236 μm . CDs synthesized at 160 °C exhibited more consistent, rigid morphologies and were evenly distributed, with particle sizes ranging from 0.189 μm to 0.351 μm . The particle sizes were estimated from the SEM images using ImageJ software, with measurements calibrated against the provided scale bar. Multiple particles were analysed to determine the representative size range. Despite being slightly larger than the 200 °C CDs, their well-defined shape and lower degree of agglomeration enhanced the exposure of functional groups and improved accessibility to active adsorption sites. This morphology contributed positively to their performance in lead(II) removal. The observed trend in morphology with respect to synthesis temperature is consistent with findings reported by Chu et al. (2019) and Wu et al. (2015). Previous studies have established that a reduction in particle size was caused by an increased reaction temperature (Chu et al., 2019). In support of this evidence, Wu et al. (2015) imply that a rise in reaction temperature caused the CDs size to shrink and its lattice structure to alter. Dehydration, polymerization, aromatization, and carbonization were the essential steps in the hydrothermal process. Thus, the higher reaction temperature favoured carbonization, which indicates the reaction occurred more thoroughly at such rising temperatures and had more condensed carbon structure and decreased in size. Taken together, these findings indicate that the 160 °C CDs exhibited a larger and more uniform particle size compared to the 200 °C CDs, while maintaining a well-defined, structured morphology. This characteristic is significant, as a slightly larger and more uniform particle size enhances surface functional group accessibility

and reduces aggregation, both of which contribute to better interaction with lead(II) ions. In this study, the 160 °C CDs demonstrated superior adsorption performance, suggesting they are more favourable for membrane-based heavy metal removal applications.

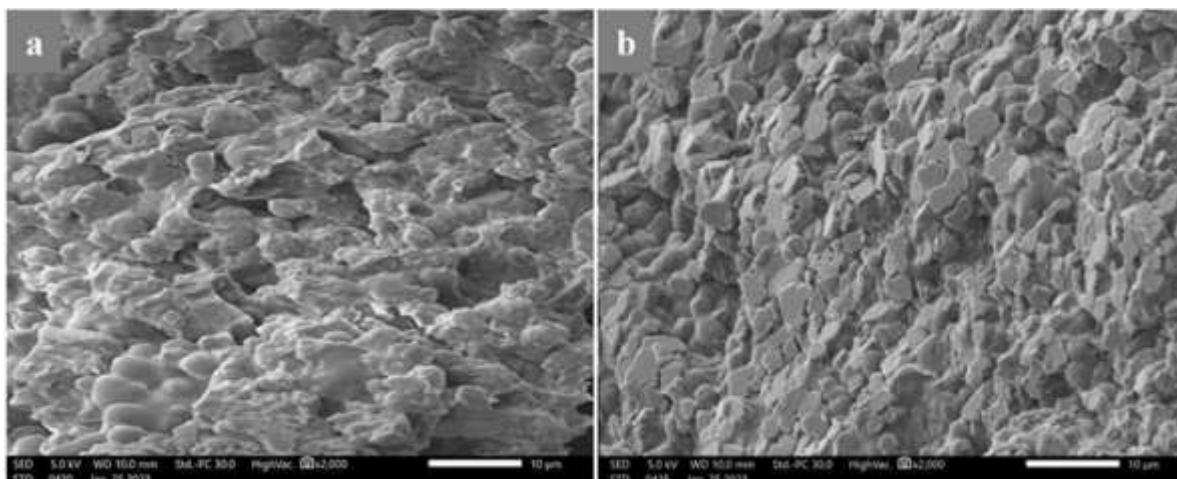


Figure 4.3: The SEM images of synthesized carbon dots (CDs); (a) 200°C and (b)160°C

4.1.4 X-ray diffraction analysis (XRD)

The crystalline structure of the synthesized carbon dots (CDs) was examined using X-ray diffraction (XRD). This technique provides insight into the atomic arrangement and degree of crystallinity of the samples, which are important factors influencing their adsorption behavior. The XRD pattern of 200 °C and 160 °C CDs (Fig. 4.4) displays a distinct broad peak at 20.04° suggested highly disordered carbon atoms with a mainly amorphous structure. This is consistent with the previous study by Bhaisare et al. (2015) which related to carbon dots synthesis via microwave-assisted synthesis from citric acid. According to the facts from Pal et al. (2020), CDs that prepared through hydrothermal treatment from carbon sources such as biomass waste, polysaccharides, food ingredients, amino acids, basically displayed an amorphous CDs system associated with broad hump between $2\theta = 15\text{-}35^\circ$ in powder XRD pattern. This broad peak corresponds to the (002) plane

of disordered graphitic carbon, indicating a turbostratic arrangement where carbon layers are stacked irregularly. The peak position at 20.04° reflects a larger interlayer spacing (~ 0.44 nm), consistent with amorphous structures. As illustrated in Figure 8, a broader diffraction pattern for the 200°C CDs compared to the 160°C CDs can be observed around 18° , which indicates their more amorphous nature.

This observation is consistent with the study by Liu et al. (2012), which reported that peak broadening is generally associated with decreased crystallite size. This trend also aligns with the SEM results, which revealed that the CDs synthesized at 200°C were less crystalline than those synthesized at 160°C . So, a greater crystallite size may be indicated by a higher peak intensity as achieved (7534 cps) through 160°C CDs at 20.04° in compared to 200°C CDs (7060 cps). This suggests that the 160°C CDs possessed better crystallinity than the 200°C CDs. In the context of this study, the improved crystallinity of the 160°C CDs could enhance structural stability and active site accessibility, supporting their superior performance in lead(II) adsorption. As mentioned in the previous study, the XRD patterns on Fig.4.4 corresponds to the arrangement and spacing of atoms in the CDs crystal lattice. This pattern corresponds to the atomic arrangement and interlayer spacing in disordered carbon dots, where loosely packed graphene-like sheets exhibit poor crystallinity.

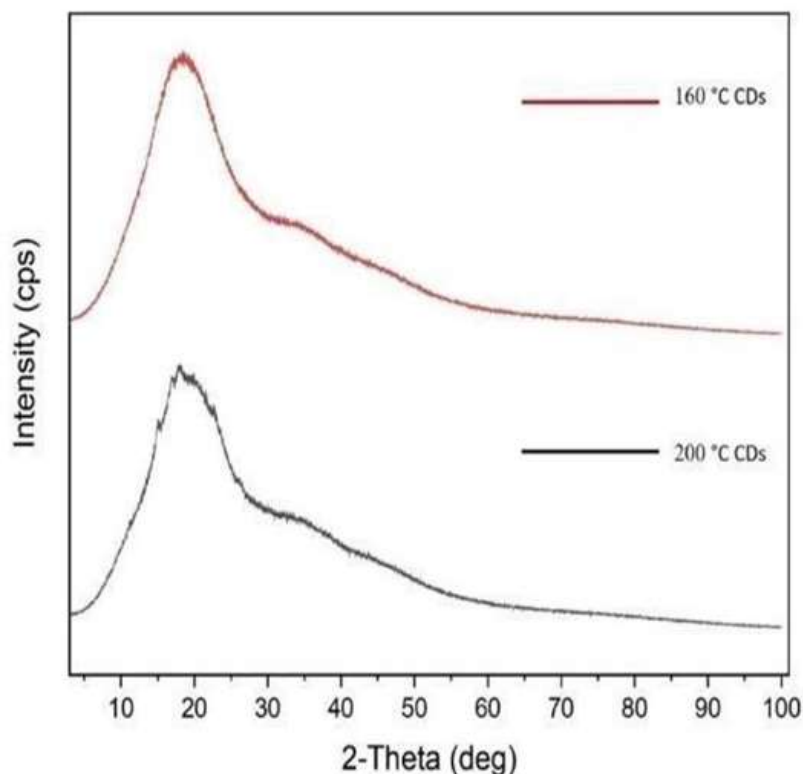


Figure 4.4: The XRD graph of 200 °C and 160 °C CDs

4.2 Characterization of Carbon Dots ZIF-8 Membrane (CDs@ZIF-8)

4.2.1 Fourier transformed infrared (FTIR)

FTIR analysis of the existence of functional groups in CDs@ZIF-8 membranes is depicted in Fig. 4.5 To confirm successful interaction of CDs and ZIF-8, FTIR analysis was performed for CDs@ZIF-8 composites on the alumina membrane. Through the FTIR spectral, the surface hydrophilic functional groups of CDs were determined. The hydroxyl (OH) molecule is linked to the broad stretching bond at 3400 cm^{-1} (Koulivand et al., 2020). The carbonyl (C=O) stretching of the -COOH group and the stretching vibration of the sp^2 hybrid carbon-carbon (C=C) stretching vibrations, respectively, are indicated by the bonds at 1730 cm^{-1} and $1640\text{-}1620\text{ cm}^{-1}$ (Koulivand et al., 2020; Wei et al., 2021). Bands at 1400 and 1230 cm^{-1} showed the presence of carboxyl (C-OH) and epoxy (C-O) functional groups

stretching vibrations from –COOH groups of the samples can be observed, correspondingly (Aliyev et al., 2019). The FTIR spectrum of 160 °C CDs@ZIF-8 membrane (red line) significantly different compared with the 200 °C CDs@ZIF-8 membrane (black line), which exhibited a two medium stretching peak at 1250-1020 cm^{-1} . In contrast, the high reaction temperature resulted the highly carbonized lattice structure of 200 °C CDs@ZIF-8 membrane and the decrease of hydrophilic groups (Wu et al., 2018). In a nutshell, accord with the expand in the carbonization degree (temperature) of the CDs synthesis, gradual rises in the absorption of C-H and C=O and declines in the absorption of N-H, C-NH-C and epoxy groups become apparent, respectively (Dai et al., 2019).

Additionally, the hydroxyl stretching and bending bands can be found at 3325 cm^{-1} and 1637 cm^{-1} , respectively, the peak at 2222 cm^{-1} and 2240 cm^{-1} is the N-H stretching vibration in imidazole rings and assigned to the vibration of the C–N bond, on ZIF-8 alumina membrane spectrum (blue line) (Zhang et al., 2019; Shahmirzaee et al., 2020). The Zn-N stretch mode produced the 421 cm^{-1} distinctive peaks. Also, the N-H vibrations of the 2-methylimidazole (Hmim) stretching and bending have been accountable for the peaks at 1591 cm^{-1} and 1681 cm^{-1} . The peaks 3135 cm^{-1} were contributing to the aromatic and aliphatic C–H stretches (Wu et al., 2021). The successful loading of CD@ZIF-8 onto the alumina membrane is supported by the FT-IR spectra, which display all the significant absorption bands characteristic of both CDs and ZIF-8. This result is consistent with the way FTIR spectra of comparable CDs and ZIF-8 based nanocomposites have been interpreted in the literature (Koulivand et al., 2020; Wu et al., 2021) while can be proved as successfully prepared in this research. Furthermore, a band related to the Zn-N stretching vibration of ZIF-8 was identified at 421 cm^{-1} in the FTIR spectrum of the CDs-modified membrane.

These FTIR results confirm that strong interactions occurred between ZIF-8 and CDs, likely through coordination bonds.

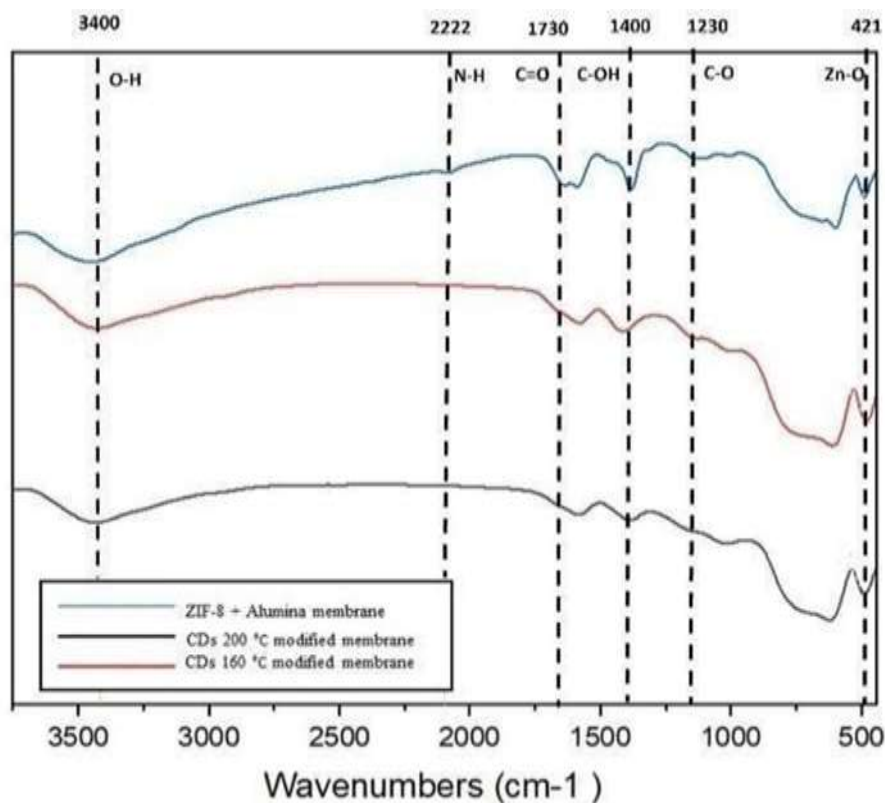


Figure 4.5: FTIR images of 200 °C and 160 °C CDs@ZIF-8 membrane spectra

4.2.2 Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX)

Fig. 4.6 shows the SEM pictures of the generated membranes' surface and cross-sections. As is apparent, the surface (Fig. 4.6a) and cross-section (Fig. 4.6b) of unmodified alumina hollow ceramic membrane display a smooth and clearly distinguishable appearance compared to the carbon dots (CDs) modified membrane as shown in (Fig. 4.6d and 4.6g). These results are similar to those reported by Manawi et al. (2022b), where the unmodified membrane exhibits a smooth structure with voids forming the Al_2O_3 membrane's pores. The Al_2O_3 membrane's cross-section image demonstrates its homogenous structure and no

presence of flaws. This consensus with the previous research that stated the membrane surface of relatively pristine surface to a less diffuse and concentrated structure before any coating and modification (Li et al., 2019). As the ready-made hollow fiber membrane had been adapted from the study by Awang Chee et al. (2021), the high permeability of the membrane was also visible in the surface image of the alumina hollow fiber (Fig. 4.6a) and revealed that the membrane has a finger-like arrangement on both its shell and lumen sides (Fig. 4.6g).

Throughout the SEM images, Fig. 4.6b and 4.6c revealed that the modified membrane prepared at different synthesis temperature brought definite dissimilar morphology on the surface of membrane. The modified membrane that constructed at 200 °C formed layer with no rhombic dodecahedron shape. The 160 °C CDs@ZIF-8 membranes, on the other hand, has the rhombic dodecahedron shape. The stable equilibrium morphology of ZIF-8 is a rhombic dodecahedron (Awang Chee et al., 2021) and provides a more active site for adsorption than the cube shape in accordance with (Linder-Patton et al., 2018). To enhance the attachment of ZIF-8 crystals onto the alumina hollow fibre membrane, a surface modification step was carried out using a silane coupling agent. In this study, APTES was employed to functionalize the membrane surface, providing amine groups that facilitate the nucleation and growth of ZIF-8. Since APTES can successfully improve the heterogeneous nucleation of the ZIF-8 crystals, it allows ZIF-8 to grow more efficiently on the surface of the APTES-modified alumina hollow fibre membrane. Moreover, this modification increases the membrane's surface hydrophobicity, promoting the development of the hydrophobic ZIF-8 layer according to the "like grows like" concept (Awang Chee et al., 2021; Wu et al., 2018).

In contrast, the modified layer is distinctly visible in the SEM images of the surface and cross-section of the CDs-modified membrane (Fig. 4.6e, 4.6f, and 4.6h, 4.6i). As seen, the encapsulation layer of the CDs@ZIF-8 membrane is clearly distributed around the membrane matrix, indicating uniform deposition. The compatibility of ZIF-8 with the alumina hollow fibre membrane has been studied and proven to be a successful combination based on previous studies (Awang Chee et al., 2021; Mahpoz et al., 2020). The ZIF-8 membranes were efficiently synthesized by using in situ solvothermal approach with APTES as the linker. The APTES layers on alumina support considerably impacted the formation of the ZIF-8 layer on the alumina support. ZIF-8 membranes made using the in-situ solvothermal method have greater crystallinity compared to membranes made using the layer-by-layer technique (Awang Chee et al., 2021). In addition, the importance of encapsulating other composites such as carbon dots in ZIF-8 pores structure of the alumina membrane matrix and their role in the improvement of the performance of the membrane was reported in literature (Gao et al., 2020b). Figures 4.6f and 4.6i illustrate clear morphological differences in the thickness of the membrane layers. The CDs@ZIF-8 membrane synthesized at 160 °C formed a thicker and more uniform layer (0.392 μm) on the alumina surface, whereas the membrane synthesized at 200 °C exhibited a thinner layer of 0.274 μm . The 160 °C CDs@ZIF-8 membranes showed an uneven and variable ridge-and-valley surface structure (Fig. 5f) while the 200 °C CDs@ZIF-8 membrane was relatively less thick and dense on the outermost surface (Fig. 4.6e). The 160 °C CDs@ZIF-8 membranes showed an uneven and variable ridge-and-valley surface structure (Fig. 4.6f), while the 200 °C CDs@ZIF-8 membrane was relatively thinner and less dense on the outermost surface (Fig. 4.6e). The greater thickness observed in the 160 °C membrane is significant, as it may contribute to a higher number of active adsorption sites and improved

structural durability, both of which are beneficial for enhanced lead(II) removal performance. This variation in thickness highlights the influence of synthesis temperature on membrane formation and structural integrity.

EDX analysis was employed to describe the elemental chemical compositions and purity of CDs modified membrane. Fig. 4.6g presents the EDX spectrum of the pristine alumina membrane, while Fig. 4.6h and Fig. 4.6i show the spectra for the 200 °C and 160 °C CDs@ZIF-8 membranes, respectively. Both of CDs@ZIF-8 membranes surface exhibits the presence of carbon, oxygen, aluminium, zinc, and silicon. In spite of that, nitrogen element is only be detected on the outer surface of 160 °C CDs@ZIF-8 membranes validating the formation of a uniformly dispersed coating and modification on the surfaces. Additionally, the formation of the ZIF-8 compound contributed to the presence of zinc and nitrogen elements, confirming successful membrane modification. Regarding the CDs, the elemental composition of carbon (C), oxygen (O), and nitrogen (N) in the CDs@ZIF-8 layer on the membrane confirms the presence of carbon dots, based on the elemental profile reported by Asmaa (2021). The EDX mapping also corroborates the distribution of carbon and oxygen in the 200 °C CDs@ZIF-8 membrane. However, nitrogen was not detected, possibly due to the dense and aggregated structure of the layer, which may have hindered a uniform distribution (Fig. 4.6f). From the EDX mapping on the well- distributed layer 160°C CDs@ZIF-8 (Fig. 4.6i)., the following elemental composition can be clearly recognized (39.36% C, 33.79% O, 7.77% N), which constructed the structure of CDs that induced different functional groups on the surface of CDs, including carbonyl, carboxyl, hydroxyl, and amino (Yadav et al., 2023).

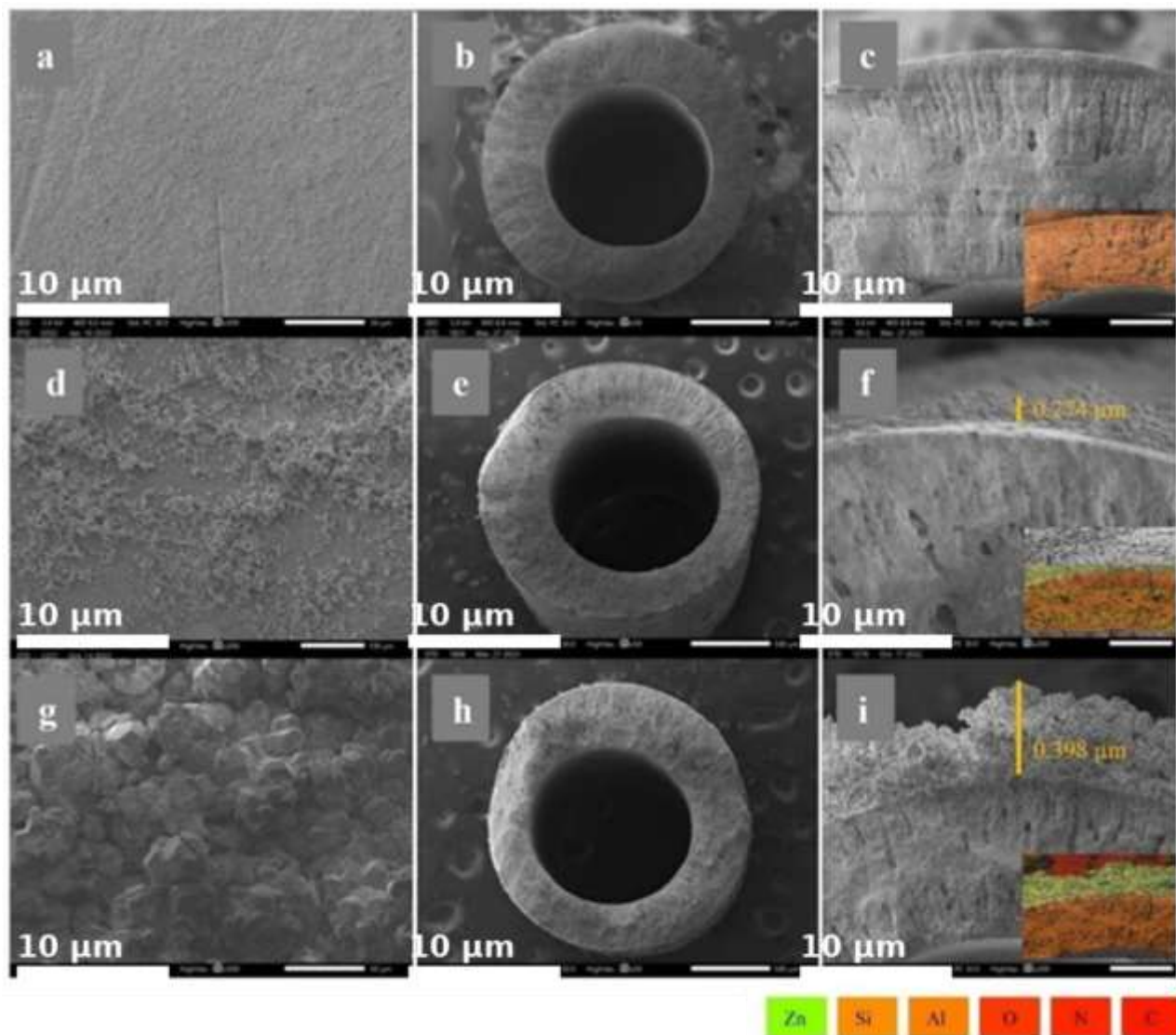


Figure 4.6: The SEM images of surface, cross-sectional, EDX-mapping of unmodified alumina membrane (a,b,c), 200°C CDs@ZIF-8 membrane (d,e,f) and 160°C CDs@ZIF-8 membrane (g,h,i).

4.3 Performance study for lead(II) removal by ZIF-8/CDs membrane

4.3.1 Batch adsorption study on lead(II) removal

The adsorption study was carried out using the batch adsorption method which was previously described by (Muhamad et al., 2018; Awang Chee et al., 2021). About 100 mL of an aqueous sample containing 5 ppm of lead(II) had 0.10 g of membrane sample at room

temperature, while being shaken at 150 rpm. In this study, initial concentration, initial pH value, and contact duration were changed to analyze lead(II) removal. The initial pH value of sample solutions was modified using 0.1 M of NaOH or 0.1 M of HCl solution. Atomic absorption spectroscopy (AAS) was used to evaluate the supernatant's lead concentration level. The relationship between absorbance and concentration of standard lead(II) solutions was plotted using calibration curves. The adsorption capacity (qe) at equilibrium (mg/g) was determined using Equation 3.0 and the removal efficiency (%) of lead(II) was determined based on the Equation 3.1 described earlier in Chapter 3.

4.3.1.1 Effect of contact time

The effect of contact duration on the removal of lead using carbon dots (CDs) modified membrane is shown in Fig. 4.7. The amount of time (in minutes) needed for the concentration of lead ions to attain equilibrium with the CDs modified membrane was used to calculate the contact time. In this study, the stirring speed was set at 150 rpm while the contact durations ranged from 0 to 540 min. The results showed that the 200 °C CDs-modified membrane achieved a removal efficiency of 65.69% and an adsorption capacity of 131.90 mg/g after 60 minutes of contact time, while the 160 °C CDs-modified membrane exhibited higher performance, with a removal efficiency of 74.73% and an adsorption capacity of 150.31 mg/g under the same conditions. The removal efficiency and adsorption capacity of the 200 °C CDs modified membrane showed a slight increase between 120 and 300 minutes, with removal efficiencies of 66.60%, 66.89%, 67.53%, and 68.48%, while the corresponding adsorption capacities of 133.20 mg/g, 133.70 mg/g, 134.71 mg/g, and 136.96 mg/g, respectively, measured at 60-minute intervals. The general pattern of removal efficiency of 160 °C CDs modified membrane claiming as of slow increasing growth with small gap of change of 81.29% (120 min) to 82.60% (180 min) and continual increase with

larger value 87.83% (240 min) and 88.16% (300 min). As regards adsorption capacity from 120 to 300 min, it is expected to increase as the removal efficiency as 133.20 mg/g, 133.77 mg/g, 134.71 mg/g, and 136.96 mg/g. When the contact duration was extended to 360 and 480 min, the removal efficiency and adsorption capacity remained consistently increased at this range for both CDs modified membrane. For the 200 °C CDs modified membrane, the lead removal efficiencies at 360, 480, and 540 minutes were 85.34%, 93.17%, and 95.72%, respectively, with corresponding adsorption capacities of 170.68 mg/g, 186.34 mg/g, and 191.43 mg/g. In comparison, the 160 °C CDs modified membrane achieved removal efficiencies of 92.87%, 95.25%, and 95.59%, with adsorption capacities of 185.77 mg/g, 190.50 mg/g, and 191.18 mg/g at the same time intervals. At 540 minutes, both membranes showed a slight decrease in performance, with the 200 °C CDs membrane dropping to 93.81% removal efficiency and 187.62 mg/g adsorption capacity, while the 160 °C CDs membrane declined to 93.75% and 187.50 mg/g, respectively. It is forecasted that the adsorption capacity remains not change if the contact time further lengthened because the adsorption of lead(II) already reached an equilibrium at time of 480 min. The adsorption pattern seen in Fig. 4.7 was caused by an initial fast sorption process aided by a rapid adsorption process that took place on the CDs modified membrane surface. The penetration of lead(II) ions deep into the adsorbent's pores caused the adsorption rate to significantly drop as the sorption process progressed (Banerjee et al., 2019), and eventually it is expected that the adsorption curves maintained a decreasing shape, suggesting nearly full saturation of the sorption sites.

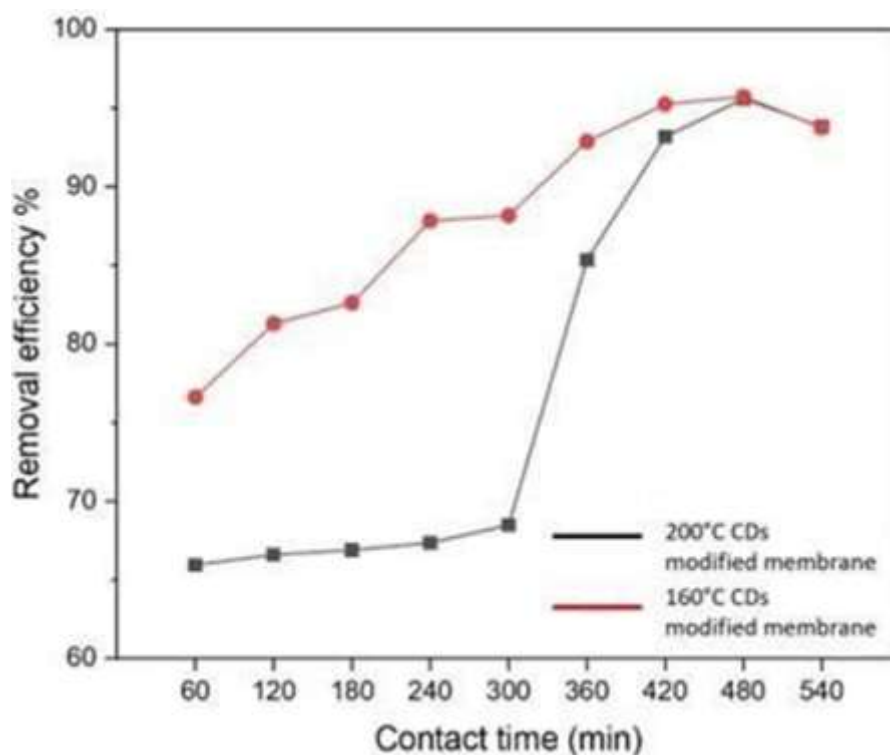


Figure 4.7: Effect of contact time on the lead(II) removal using carbon dots 200°C (black and 160°C (red) modified membrane

4.3.1.2 Effect of pH

The pH of the aqueous solution is among the most important variables that control the amount of heavy metals and how significant the removal percentage is by influencing the adsorbent surface binding sites including their activity and protonation mechanism, together with the solution chemistry and solubility of metal ions (Darweesh et al., 2022). Fig.4.8 shows the effect of pH on the efficiency of CDs modified membrane in removing lead ions from synthetic aqueous solution. The study was focused on the 3 different pH 4 (acid condition), pH 7 (neutral condition) and pH 10 (alkaline condition). As a result, it is thought to be crucial to establish the ideal pH for adsorption since the ionic groups may have an impact on electrostatic interactions, which might alter the chemical equilibrium of the solution's components (Filachowski, 2018). The rate of removal of lead(II) might be related

to the influences of pH. The findings showed that the lead(II) removal efficiency of the 160 °C CDs modified membrane increased steadily with pH, reaching a maximum of 98.02% at pH 10 (Fig. 4.8). The figure also implied that the removal of lead(II) by 160°C CDs modified membrane reduces with the decrease of pH value at the lower pH.

At pH 4, the adsorption percentage is small because of the competitive interaction between H^+ and Pb^{2+} for the adsorbents' exchange site (Awang Chee et al., 2021). According to Jeferson et al. (2020), this phenomenon results from the hydroxide (OH^-) and hydronium (H_3O^+) or hydrogen (H^+) ions being in equilibrium at pH 7. While in an acid solution, metal ions and H^+ ions compete more strongly for the active area on the adsorbent surface. As a result, at low pH, the functional groups on the surface of the adsorbent are mostly linked to H^+ , which hinders the retention process due to repulsive forces caused by the positive charges on the metal ions. Conversely, a higher pH may favour adsorption since a higher pH result in a lower concentration of H^+ . On the other hand, a high pH might result in the precipitation of certain metals, which also prevents adsorption (Cruz-Lopes et al., 2021).

Despite that, not many metals react to changes in pH in the same way; for certain metals, such as nickel and lead, adsorption increases as the pH rises, and the maximum adsorption is seen right before precipitation takes place. In contrast, for the other metals, such as chromium(VI), adsorption is not associated with precipitation (López et al., 2000). Because of the increased concentration and greater mobility of H^+ ions present, which compete with lead(II) ions for sorption sites in the membrane and become favoured for binding sites adsorption, the minimal lead adsorption and removal percentage that results at low pH (pH 4) may be explained. Hydrogen ions (H^+) could surround the surface of the membrane at lower pH values, preventing lead(II) ions from reaching the membrane's

binding sites. As an outcome, there is less attraction between the lead(II) ions and the adsorbent.

Contrarily, as the pH rises, a larger amount of negatively charged membrane surface becomes accessible, promoting greater lead adsorption. During the complexation process, lead(II) ions demonstrate strong and stable binding to the functional groups present on the membrane surface (Darweesh et al., 2022). In the same vein, lowering pH content reduces the concentration of H^+ , which lessens the competition between protons and metal ions for adsorption sites on particle surfaces. The rising pH, which promotes metal ion precipitation in the form of hydroxides from the solution, is another factor that might help to enhance metal ion adsorption. The slowdown in adsorption that was noticed after pH 10 is caused by the formation of soluble hydroxyl complexes(Adeolu et al., 2016). In addition, the results obtained agreed with the declining patterns of adsorption was observed at pH 13 in 160 °C modified membrane, showing the reduction in vacant adsorption sites on the sorbent sides (Gollakota et al., 2021).

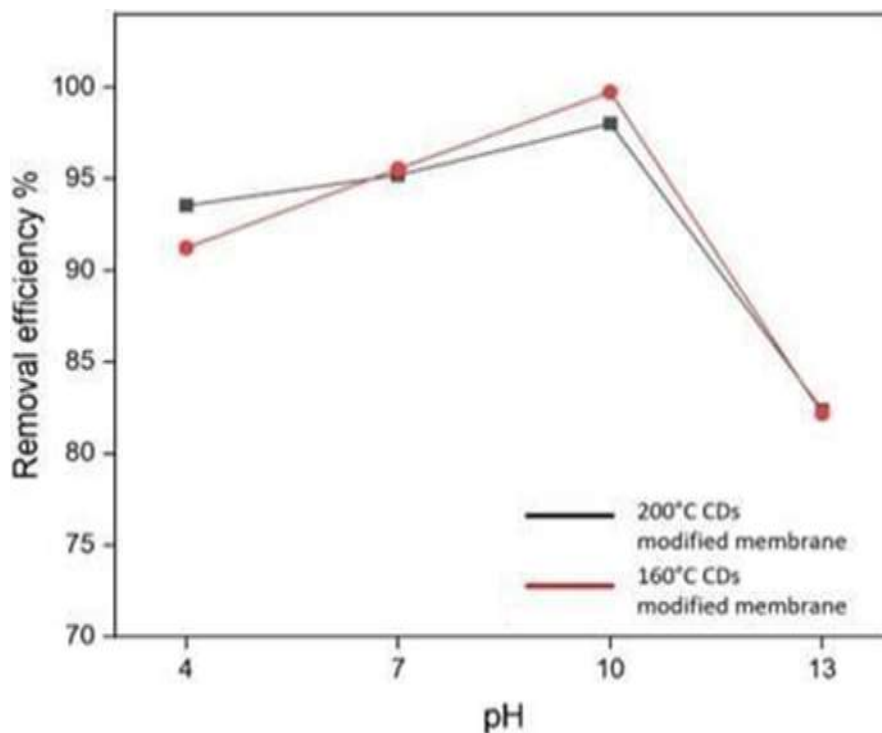


Figure 4.8: Effect of pH on the lead(II) removal by CD@ZIF-8 membrane

4.3.1.3 Effect of initial concentrations

Fig. 4.9 shows the adsorption capacity of the carbon dots modified membranes at different initial concentrations of aqueous solution of lead(II) nitrate. The adsorption capacity of lead increased when the initial concentration of Pb was increased from 0 to 100 mg/L for 160 °C CDs modified membrane. This study aligns with the findings of Muhamad et al. (2018), who utilized supported zeolite-Y membranes as adsorbents for the removal of nickel from aqueous solutions in a batch sorption process. The result demonstrates that each CDs modified membrane sample's adsorption capabilities increase with increasing lead starting concentration. Pursuant to the Fig. 4.9, the 160°C CDs membranes reached their highest adsorption capacity of 95.16 mg/g. It is anticipated that the removal efficiency of lead is proportional to the increment in initial lead concentration because of the larger driving force present at the bulk concentration gradient (Alqadami et al., 2018). At lower

concentration of lead(II) ions, the number of lead(II) ions which are available in the solution is smaller in contrast to the available number of areas on the adsorbent. However, at higher concentrations, the available sites for adsorption become lesser and the percentage removal of lead(II) ions relies on the initial concentration (Fouda- Mbanga et al., 2020). In a recent article in by Tee et al. (2022) points out that the adsorption capacity declined when the initial concentration achieved their limit. It is clear when the initial concentration exceeded 100 mg/L until 200 mg/L, the adsorption capacity did not rise further, indicating that the saturation of adsorption sites on the surface of the 160°C CDs modified membrane could not support a greater concentration of lead(II).

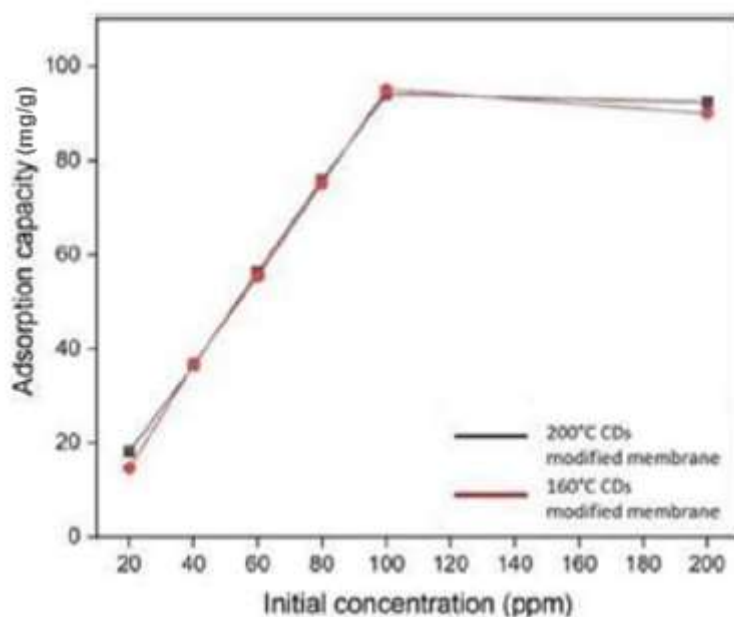


Figure 4.9: Adsorption capacity of carbon dots modified membrane membranes at different initial concentrations

4.3.2 Adsorption isotherm

Adsorption isotherm is the relationship between the amount of solute adsorbed in equilibrium at a fixed temperature and the concentration of solute in the solution. The metal absorption per unit mass of adsorbent (q_e) and the equilibrium adsorbate concentration (C_e) in the bulk fluid phase are related by the adsorption isotherms. The Freundlich and Langmuir isotherms of adsorption are typically used to describe the distribution pattern of metal ions between phases (Muhamad et al., 2018). Langmuir and Freundlich isotherms were used to study the sorption mechanism. When molecules are adsorbed as monolayers on an adsorbent surface on entirely homogenous surfaces with minor interaction between them, the Langmuir isotherm is applicable. Freundlich could be an option for heterogeneous surfaces and multilayer sorption. Langmuir and Freundlich are correspondingly represented in Equations 4.0 and 4.1.

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \quad \text{Equation 4.0}$$

$$q_e = K_f C_e^{1/n} \quad \text{Equation 4.1}$$

K_L : the Langmuir adsorption constant

q_e : the equilibrium adsorption capacity (in mg/g)

q_m : the adsorbent's maximum adsorption capacity (in mg/g)

K_f : the Freundlich adsorption constant

C_e : the equilibrium concentration (in mg/L)

n : the heterogeneity factor

4.3.3 Kinetic study

Next, the first-order and second-order adsorption kinetics were applied to determine the reaction orders depending on the adsorbent's capacity, as shown in Equation 4.2 and 4.3, correspondingly. The following equation of pseudo-first order was used:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{Equation 4.2}$$

The intercept and slope of the linearity for the plot of $\log (q_e - q_t)$ vs t can be used to determine the values of q_e and k_1 for the pseudo-first-order model. While for the pseudo-second order equation:

$$\frac{1}{q_t} = \frac{1}{K_{2p} q_e^2} + \frac{1}{q_e} t \quad \text{Equation 4.3}$$

Plotting t/q_t ($\text{min g}^{-1} \text{mg}^{-1}$) and t (min) yielded pseudo-second order. Slope and intercept were used to derive q_e and h , respectively.

q_e : the amount of metal ions adsorbed (adsorption capacity) at equilibrium (mg/g)

q_t : the amount of metal ions adsorbed (adsorption capacity) at time t (mg/g)

t : time (min)

k_1 : equilibrium constant for first-order (min^{-1})

k_2 : equilibrium constant for second-order ($\text{g mg}^{-1} \text{min}^{-1}$)

Table 4.1: Adsorption isotherm and adsorption kinetic study for lead(II) adsorption on CDs@ZIF-8 membrane

Adsorption isotherm model			
Langmuir		Freundlich	
q_m (mg/g)	0.09	1/n	1.42
K_L (L/mg)	-0.13	K_F (L/g)	7.28
R^2	0.86078	R^2	0.97548
Kinetic Study Order			
First Order		Second Order	
q_e (mg/g)	34.94	q_e (mg/g)	100.60
K_1 (min^{-1})	-0.00002	K_2 ($\text{g mg}^{-1}\text{min}^{-1}$)	0.00033
R^2	0.79126	R^2	0.99652

Table 4.1 displays the data for the lead(II) ion adsorption investigation on CDs@ZIF-8 hollow fiber ceramic membranes, along with a kinetic study and isotherms. At pH 10, an adsorption test was conducted over a concentration range of 20–200 ppm for 8 hours. The data demonstrated the effectiveness of lead(II) adsorption onto the CDs-modified membrane. The lead(II)'s adsorption mechanism was great fitted, with an R^2 value of Freundlich model linear equation, 0.995, in contrast to the Langmuir model's R^2 of 0.989 which is 0.28187. It appeared that the Freundlich model explained the emergence of lead(II) adsorption multi-molecular layer on a heterogeneous surface (Uddin et al., 2021). The value of 1/n represents the tendency of adsorption through the amount of adsorbate that is adsorbed onto the adsorbent or surface heterogeneity (Khandelwal et al., 2020). The value of 1/n shows whether the sorption process is irreversible ($1/n = 0$), unfavourable ($1/n > 1$) and favourable ($0 < 1/n < 1$) (Erdogan, 2019). If its number is closer to zero, the surface is more heterogeneous (Awang Chee et al., 2021). The results of this adsorption study's results indicate that the CDs@ZIF-8 modified membrane surface is more heterogeneous, with $1/n = 0.2396$. This

$1/n$ value in other words demonstrated heterogeneous surface, favorable, and normal adsorption (Nandiyanto et al., 2020). The numbers of the Freundlich constant (n) may be used to assess the adsorption process (Awang Chee et al., 2021): n is greater than 1, the adsorption entails chemical interaction; however, if n is less than 0, physical interaction did occurred. If n equals 1, there is unlikely to be adsorption. The interaction between lead(II) and the CDs@ZIF-8 membrane in this research could be categorized as a chemisorption process since the value of n was 3.89. The Langmuir isotherm graph as well as the Freundlich isotherm are shown in Fig. 4.10.

This research used pseudo-first order and pseudo-second order models to figure out the adsorption mechanism of lead(II) by the CDs@ZIF-8 membrane. Fig. 4.11 displays the pseudo first-order and pseudo second-order kinetic graph. The linear plot and the satisfactory values of correlation coefficients (R^2) suggested the conformity between the model-predicted value and experimental data. In cases where R^2 values are near to, equal to, or significantly bigger than 1, the model for lead(II) adsorption is more appropriate (Musie and Gonfa, 2022). This study results for the correlation coefficient (R^2) value of 0.99652 reviewed that the adsorption kinetics of the CDs@ZIF-8 membrane is better fitted the pseudo-second-order model rather than the pseudo first-order model. Therefore it can be said that the pseudo-second-order kinetic model accurately describes the mechanisms lead(II) ions adsorb on the CDs@ZIF-8 membrane. Furthermore, the theoretical q_e from the pseudo-second order model was also relatively near to the experimental number.

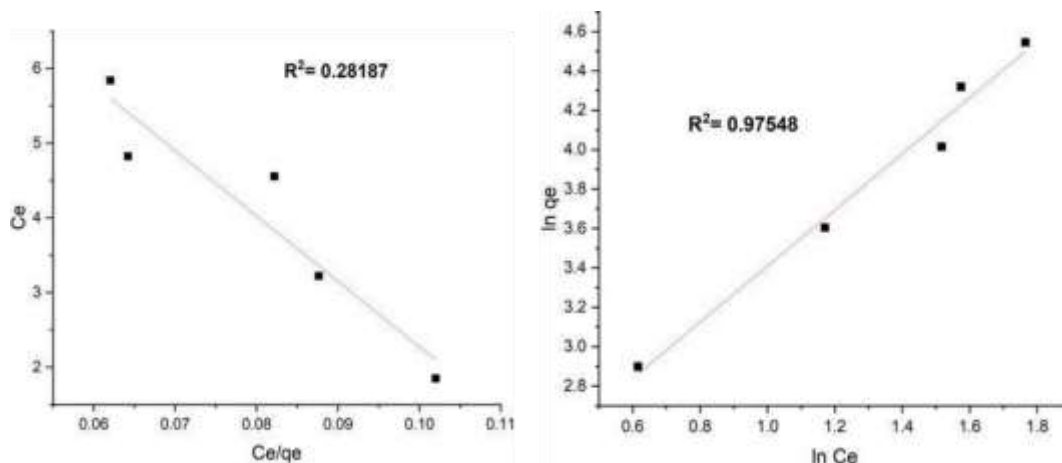


Figure 4.10: Langmuir model (left) and Freundlich model (right)

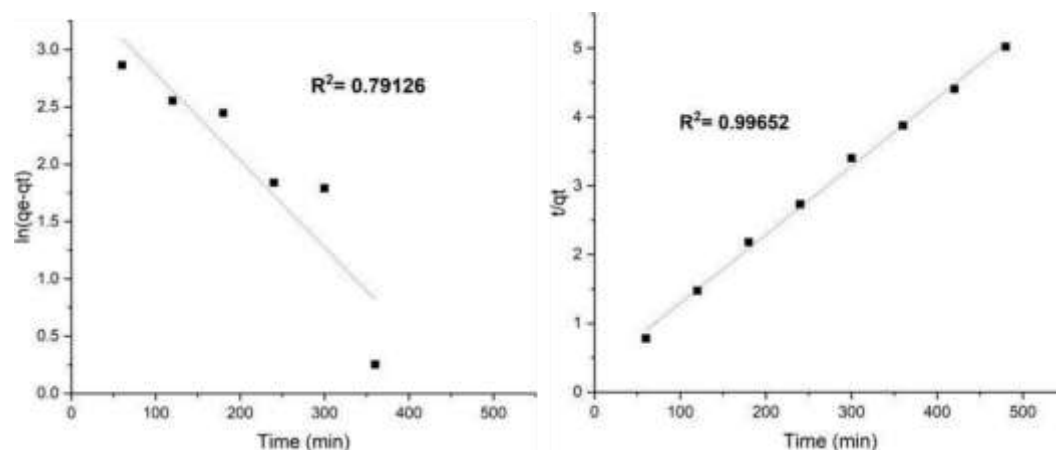


Figure 4.11: First order (left) Second order (right)

4.3.4 Filtration study

The application of CDs@ZIF-8 membranes was further assessed by conducting filtration study at significant transmembrane pressure (TMP) (1 bar) by employing a cross-flow filtration system. To confirm the performance of the CDs@ZIF-8 membranes, pristine alumina hollow fiber was tested as a control. Fig. 4.12 illustrates the membrane's performance in terms of water flux and lead(II) ion removal capability. According to the data of lead(II) removal and water flux of the modified membrane revealed that the 160 °C

CDs@ZIF-8 membrane offered higher rejection value towards lead(II) (74.73%) together with 38.55 L/m² h water flux. Among of all the investigated membranes, the sample of the 160°C CDs@ZIF-8 membrane had the greatest flux, and rejection of lead(II) compared to the 200 °C CDs@ZIF-8 membrane and the pristine alumina membrane. For the 200 °C CDs@ZIF-8 membrane, the measured flux was approximately 19.03 L/m² h, accompanied by a lead(II) rejection efficiency of 72.79%. This phenomenon is due to the uniform distribution of CDs@ZIF-8 composite layer as can be seen from the SEM images, that demonstrated excellent antifouling and the higher pure water flow. This was attributed to the development of a hydrophilic and more porous membrane (Saraswathi et al., 2020). Nonetheless, by reducing the thickness of CDs@ZIF-8 layer to 160°C CDs@ZIF-8 membrane, it is expected to lead a higher observed permeation flux of the membrane. Prior studies that have noted that by simply decreasing the thickness of the separating layer, the porosity of the membrane was enhanced and decrease in water resistance in the modified membrane matrix (Zhang et al., 2020). Additionally, the pore size of the membrane separation layer plays a major role in determining the rejection ratio (Wang et al., 2019). For that reason, it is crucial to modify and regulate the structural morphology and pore size in order to enhance the performance more efficiently.

Regarding membrane hydrophilicity, the encapsulation of CDs within the ZIF-8 pores introduced a significant number of –OH functional groups on the ZIF-8 nanoparticles. This contributed to the hydrophilic nature of the membrane, thereby enhancing its permeability. The membrane's higher hydrophilicity boosted the capacity of water molecules to absorb within the membrane matrix (Peechmani et al., 2021). The performance of the CDs@ZIF-8 composite as a selective active layer has been demonstrated in previous studies, where it was shown to enhance solute adsorption without significantly affecting the water

flux of the membrane, owing to the unique pore structure of ZIF-8 (Wang et al., 2019). Interestingly, the presence of non- polar groups (CH_3) in ZIF-8 contributes to high water flow and generates a hydrophobic framework with weak affinities for water molecules (Mahpoz et al., 2019). Hence, as opposed to pore size, water flow was also influenced by the functional group polarity of ZIFs. On the flip side, the pristine membrane unable to reject the lead(II) ions sufficiently as the other modified membrane with a lower lead(II) ions removal, 64.56% in conjunction with $12.05 \text{ L/m}^2 \text{ h}$. An alternative explanation for this result is that it is due to the high porosity of membrane and average pore size, which are larger than the lead(II) ion (Awang Chee et al., 2021). The decreasing of heavy metal ions rejection like lead(II) ions were linked to the possibility of nanoparticle agglomeration at high concentrations, thereby lowering the efficiency of the surface of the nanoparticles and the number of accessible adsorption sites. Therefore, having a suitable amount and possessing nanoparticles that are evenly distributed allows the membrane to reject more lead(II) ions (Zareei and Hosseini, 2019). As the pristine alumina hollow fiber lacked a selective layer barrier on its outer side, it could not to prevent the solute in the draw solution from flowing through into the feed solution deriving in poor separation performance (Mahpoz et al., 2019).

In view of all that has been mentioned so far, the possible reason for the variable performance of the membranes is not solely on the variation in membrane thickness, however, the factor such as the uniform distribution of modification separation layer also demonstrated pivotal effects. From the results obtained, the relationship between flux and lead(II) rejection is directly correlated. This is consistent with the work by Saraswathi et al. (2020), which reported that the surface morphology of the modified membrane showed a uniform distribution of CDs@ZIF-8 across the top skin layer, thereby facilitating improved water permeability. Secondly, the membrane's porosity and thickness are key factors in

determining the trade-off effect. Without a doubt, the CDs@ZIF-8 membrane have a dense and compact surface layer which increased the performance in rejecting ions, although the reduced water flux seen is equally unfavourable (Awang Chee et al., 2021). Together, these studies indicate that the 160 °C CDs@ZIF-8 membrane is high productivity membrane which have high permeability and flux. On account of improvement performance, the thickness of outer layer must also be regulated to lessen the resistance that hinders the water passage over the membranes. On the other hand, the pore size of the modified membrane also needs to be controlled so that the membrane could maintain the lead(II) ions and water to penetrate through the membranes. The related work on the removal of lead(II) using ceramic-based adsorptive membrane had been illustrated on Fig. 4.12.

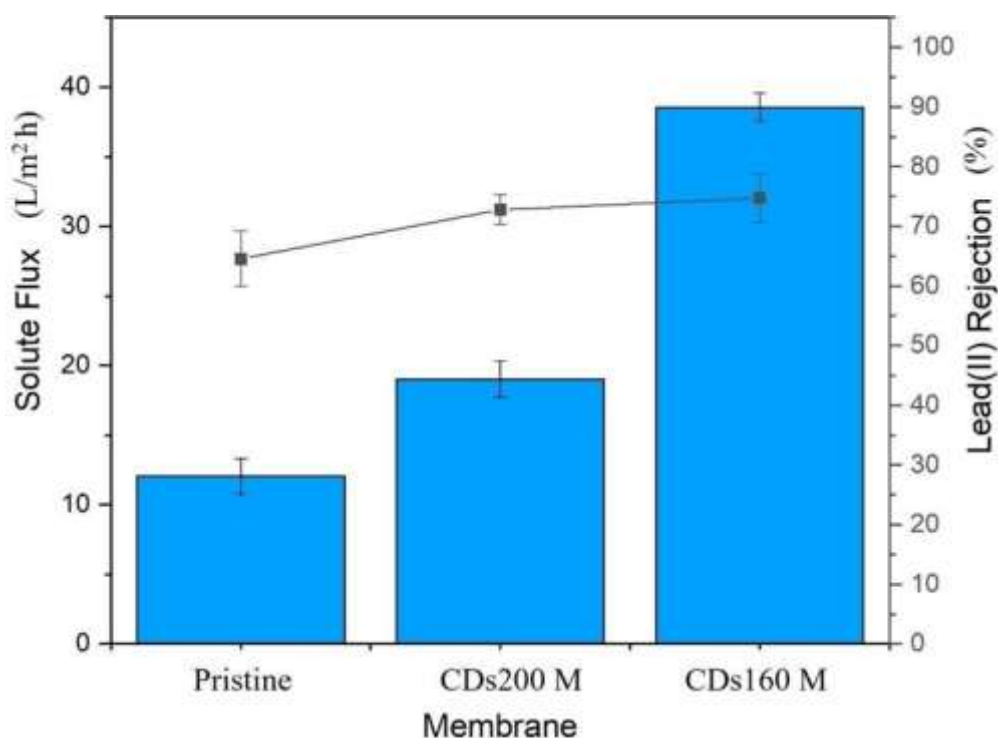


Figure 4.12: The solute flux and lead(II) rejection of CDs@ZIF-8 alumina membrane

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

A novel composite (CDs@ZIF-8) based on carbon dots and zeolitic imidazolate framework (ZIF-8) on the alumina membrane support was successfully synthesized by incorporating CDs into the pores of ZIF-8 through a simple in-situ solvothermal method. The carbon dots (CDs) were prepared from sago *hampas* via a simple hydrothermal synthesis process at two different temperatures: 200 °C and 160 °C. The 160 °C CDs displayed a more uniform morphology with less agglomeration, contributing to better surface functionality. Compared to the 200 °C CDs@ZIF-8 membrane, the 160 °C CDs@ZIF-8 membrane exhibited better adsorption performance, achieving a maximum lead(II) adsorption capacity of 95.16 mg/g. Moreover, the study revealed that pH 10 provided the most favourable condition for lead(II) adsorption onto the CDs@ZIF-8 membrane. The adsorption data fitted well to the Freundlich isotherm and pseudo-second-order kinetic model, indicating that the adsorption process occurs via multilayer interaction on a heterogeneous surface and is mainly governed by chemisorption mechanisms. The filtration of lead(II) ion solution using the 160 °C CDs@ZIF-8 membrane achieved a rejection of up to 74.73% with a water flux of 38. Lm⁻²h⁻¹, showing both high rejection and good permeability. In summary, the CDs@ZIF-8 alumina membrane presents a promising approach for lead(II) removal from wastewater, offering a dual-function platform combining adsorption and membrane filtration for efficient heavy metal treatment.

5.2 Recommendations

Research on CDs has advanced significantly because scientists have been focusing on producing CDs that have distinct qualities from various types of raw materials. In order to comprehend why synthesis affects structure and performance, we suggest that future study should focus more on the synthesis mechanisms. The precise structure of CDs is unclear due to the absence of systematic structural traits and the lack of complicated structures that would highlight these features. As a result, further research is needed on this topic. Furthermore, regeneration and reusability are crucial aspects of developing sustainable and cost-effective materials for heavy metal removal. Hence, it is recommended to build an effective regeneration technique to restore the adsorption capacity of the composite membrane and examine the CDs@ZIF-8 membrane's reusability and stability over several cycles. Researchers can learn more about the long-term effectiveness and longevity of CDs@ZIF-8 membranes for lead(II) removal in real-world application by addressing these factors in regeneration and reusability studies. Aside from that, to satisfy the requirements of larger-scale use, future research should concentrate on creating scalable and economical processes for the synthesis and manufacture of CDs@ZIF-8 membranes. Also, investigate the feasibility of applying the technology in real-world applications, considering parameters like flow rates, membrane thickness, and membrane area. Lastly, future studies should examine the effects of utilizing ZIF-8 and CDs on the environment, taking into account the composite membrane's safety features such as focusing attention to the handling and disposal.

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