Faculty of Resource Science and Technology

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 $Lm^{-2}h^{-1}$. 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 $Lm^{-2}j^{-1}$. 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*

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LIST OF ABBREVIATIONS

Ag	Silver
AgNCs	Silver Nanoclusters
Al	Aluminium
Al2O3	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
MnO2	Magnesium Dioxide
MOFs	Metal Organic Frameworks
MoS2	Molybdenum Disulfide
MWCO	Molecular Weight Cut Off
NCDs	Nitrogen-doped Carbon Dots
NEMs	Nano-enhanced Membranes
NF	Nanofiltration
NH2	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
SiO2	Silicon Dioxide
SO3H	Sulfonic Acid
TC	Thiol-Functionalized Cellulose
TFN	Thin Film Nanocomposite
Ti	Titanium
TiO2	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
ZrO2	Zirconium Dioxide
Zn	Zinc
$Zn(NO_3)_2.6H_2O$	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 m^3 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