Faculty of Engineering

ISOTHERM STUDY OF HEAVY METAL ADSORPTION BY MEMBRANE INCORPORATED WITH ACTIVATED CARBON

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Bachelor of Engineering with Honours
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ISOTHERM STUDY OF HEAVY METAL ADSORPTION BY MEMBRANE INCORPORATED WITH ACTIVATED CARBON

CORNEELIA ANAK TEDONG

A dissertation submitted in partial fulfillment

of the requirement for the degree of

Bachelor of Engineering with Honours

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Dedicated to my beloved parents, family and friends who always bestow me sustainable motivations and encouragements

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ABSTRACT

Adsorption process has widely applied in many industries to remove the heavy metals because it is more economical, environmental friendly and efficient in removing heavy metals and other pollutants. Adsorption process usually used powdered adsorbents to adsorb the heavy metals. On the other hand, membrane technology is usually applied for filtration process. Therefore, this project was carried out to create the hybrid membrane that can do both filtration and adsorption process. The aim of this work was to study the adsorption isotherm for heavy metal removal by using membrane with activated carbon. The adsorption process was verified by using isotherm models which are Langmuir, Temkin and Freundlich models. The membrane was prepared from polysulfone (PSU), N-methyl-2-pyrolidone (NMP), polyethyleneimine (PEI), silver nitrate ($AgNO_3$) and activated carbon (AC). The membrane was fabricated by using phase inversion technique by applying immersion precipitation method. The membrane that has been produced was undergo Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) for characterization. For adsorption process, the membrane was put into synthetic waste water solution which is lead (II) with known concentration for 24 hours before undergo Atomic Absorption Spectroscopy (AAS) analysis. The results were represented by using graph that have been plotted based on the equations of each isotherm model. The results showed that Freundlich was the best model to verify the adsorption of lead (II) onto membrane with activated carbon as it gives the highest R^2 value which is 0.9893.

Keywords: Adsorption, heavy metal, activated carbon, membrane, phase inversion, isotherm, Langmuir, Freundlich, AAS, SEM, FTIR

ABSTRAK

Proses penjerapan telah digunakan secara meluas dalam pelbagai industri untuk mengurangkan logam berat kerana proses ini lebih menjimatkan, mesra alam dan cekap dalam mengurangkan logam berat dan bahan pencemar yang lain. Proses penjerapan biasanya menggunakan serbuk adsorben untuk menyerap logam berat. Teknologi membran selalunya digunakan untuk proses penapisan. Justeru, projek ini dijalankan untuk mencipta membran yang boleh melakukan kedua-dua proses penapisan serta penjerapan. Tujuan projek ini dijalankan adalah untuk membuktikan penjerapan logam berat boleh dilakukan dengan menggunakan membran yang digabungkan dengan karbon diaktifkan. Proses penjerapan yang berlaku terhadap logam berat dibuktikan dengan mengunakan model-model isoterma iaitu *Langmuir*, *Temkin* dan *Freundlich*. Membran untuk projek ini akan diperbuat daripada *polysulfone* (PSU), *N-methyl-2-pyrolidone* (NMP), *polyethyleneimine* (PEI), nitrat perak ($AgNO_3$) dan karbon diaktifkan (AC). Membran ini dibuat dengan menggunakan teknik fasa balikan dengan mengapplikasikan kaedah *immersion precipitation*. Membran itu kemudian diklasifikasikan dengan mengunakan *Scanning Electron Microscope* (SEM) dan *Fourier Transform Infrared Spectroscopy* (FTIR). Untuk proses penjerapan, membran yang telah disediakan akan diletakkan di dalam air sisa sintetik iaitu cecair plumbum yang telah diketahui kepekatannya selama 24 jam sebelum menjalani analisis *Atomic Absorption Spectroscopy* (AAS). Keputusan untuk proses ini dibuktikan dengan menggunakan graf yang telah diplotkan berdasarkan formula model-model isoterma. Keputusan telah menunjukkan bahawa *Freundlich* ialah model terbaik untuk membuktikan proses penjerapan terhadap plumbum (II) menggunakan membran bersama karbon diaktifkan kerana model ini mempunyai nilai R^2 paling tinggi iaitu 0.9893.

Kata kunci: Penjerapan, logam berat, karbon diaktifkan, membran, fasa balikan, isoterma, *Langmuir*, *Freundlich,* AAS, SEM, FTIR

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ABBREVIATION

AAS	-	Atomic Absorption Spectroscopy
AC	-	Activated carbon
$AgNO_3$	-	Silver nitrate
FTIR	-	Fourier Transform Infrared Spectroscopy
GAC	-	Granular activated carbon
ICP-MS	-	Inductively Coupled Plasma Mass Spectroscopy
MF	-	Microfiltration
NF	-	Nanofiltration
NMP	-	N-methyl-2-pyrolidone
PAC	-	Powdered activated carbon
PEI	-	Polyethyleneimine
PSU	-	Polysulfone
RO	-	Reverse osmosis
SEM	-	Scanning Electron Microscopy
UF	-	Ultrafiltration

NOMENCLATURE

%	-	Percent
°C	-	Degree Celsius
mg/L	-	Milligram per liter
MW	-	Molecular weight
Ppm	-	Parts per million
wt%	-	Weight percentage
µm	-	Nanometer

CHAPTER 1

INTRODUCTION

1.1 Background of study

Waste is defined as the substances that are eliminated or discarded as no longer useful or required after completing certain processes. Waste can be divided into several categories such as domestic waste, industrial waste, chemical waste, waste water and municipal waste. However, the wastes must be treated before discharge to environment. Most of the wastes contain heavy metals which including plating wastes, spent solvents, landfill leachates and also contaminated groundwater from abandoned hazardous waste sites (Reed & Matsumoto, 1993). The presence of heavy metals have potentially affect human physiology as well as other biological systems when the acceptable limits are exceeded. Heavy metals could not be destroyed and its toxicity could affect the human and environment. Apart from that, the increasing demand of heavy metals in industries causes the increasing in availability of metallic substances in natural water sources (Karnib, Kabbani, Holail, & Olama, 2014). One of the most poisonous heavy metal is lead because acute exposure to lead may affect the gastrointestinal tract and nervous system (Imamoglu & Tekir, 2008). Apart from that, Cechinel et al. (2013) has states that constant exposure to lead will cause learning disabilities in children, damage to organs such as the liver, kidneys and heart, and immune system disorders. The lead that is released to the environment is comes from many industrial processes, such as the production of paint coatings, dyes, glass and batteries is possibly toxic to humans and aquatic environment Cechinel et al. (2013).

Common methods to eliminate heavy metal ions in the environment involve precipitation, adsorption, membrane filtration, coagulation and ion-exchange (Imamoglu & Tekir, 2008). The description of each mentioned technique is explained in the Table 1.1.

Table 1.1: Methods to remove heavy metals

Method	Description	Reference
Precipitation	Chemical precipitation technique will form undissolved precipitates due to reaction of chemicals and heavy metal ions. This technique is preferable for several processes as it is simple and affordable to carry out.	(Fu & Wang, 2011)
Adsorption	Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or adsorbent and forms adsorbate. This method is effective and economic to be implemented and usually applied in industrial applications such as water purification.	(Fu & Wang, 2011); (Lakherwal, 2014)
Membrane filtration	Membrane is a physical barrier that allows certain compound to pass through depending on their physical and/or chemical properties. The membrane processes include ultrafiltration, reverse osmosis, nanofiltration and electrodialysis.	(Fu & Wang, 2011); (Munir, 2006)
Coagulation and flocculation	The concept of coagulation process is reducing the net surface charge of the colloidal particles to be stabilized by electrostatic repulsion process. Whereby, flocculation is the process of forming bridges among the flocs by polymers and the particles are clump together into large agglomerates.	(Gunatilake, 2015); (Fu & Wang, 2011)
Ion-exchange	The ion-exchange resin has the ability to exchange its cations with the metals in the wastewater and able to attract soluble ions from the liquid state to the solid state.	(Fu & Wang, 2011); (Gunatilake, 2015)
Electrochemical treatment	Electrochemical treatment is a method of plating-out metal ions that exist on a surface of the cathode and able to recover metals in the elemental metal state. Electrochemical treatment technologies require high investment and high cost for electricity supply and thus this technique is not widely applied.	(Fu & Wang, 2011)

For large scale industries, chemical precipitation technique is the most common method applied for their treatment system which requires subsequent stages of sedimentation and filtration before the treated water can be reused (Cechinel, de Souza, & de Souza, 2013). However, this process is not appropriate for the treatment of effluents in large capacity that contain low concentrations of metal ions as its extraction process has low efficiency and expensive (Cechinel et al., 2013). Other than that, membrane filtration technology is able to eliminate heavy metal ions with high efficiency, but the drawbacks of this technology are expensive, complicated in process, membrane fouling and low permeate flux which have limited their function in eliminating the heavy metal (Fu & Wang, 2011). Many of these methods that have been mentioned in the Table 1.1 have drawbacks such as high costs associated with the installation, operation and sludge disposal and some of them are unsuitable for small scale industries (Cechinel et al., 2013; Febrianto et al., 2009).

Adsorption is one of the water and wastewater treatment methods which is globally applied for its efficiency, affordable and non-pollution (SenthilKumar, Ramalingam, Sathyaselvabala, Kirupha, & Sivanesan, 2011). Adsorption is the process where the substance which is initially exist in one phase is then transferred into another phase by accumulation at the interface between those phases (Armenante, 2000). The adsorption process is the most preferred technique for water and wastewater treatment as it offers flexibility in design and operation as well as forming great quality of treated effluent. Apart from that, adsorption process can be reversible, therefore, adsorbents can be regenerated by using appropriate desorption method (Fu & Wang, 2011). There are many types of adsorbent that can be used for the adsorption process such as silica, peanut husk, sawdust, cashew nut shell, activated carbon and many more. According to Reed & Matsumoto (1993), adsorption of metals by activated carbon can give a better performance for the treatment process. Thus, the combination of activated carbon and membrane for adsorption process is going to be investigated for this project.

Activated carbon is a type of charcoal which has being burnt or treated to increase its adsorptive power. Activated carbon acts as adsorbent for heavy metal removal (Al-Omair & El-Sharkawy, 2007). Basically, activated carbon is a carbonaceous and highly porous adsorbent that has a complex structure composed originally of carbon atoms. Activated carbons are made up from coconut shell, peat, hard and soft wood, coal and other carbonaceous specialty materials. The porosity of activated carbon is high, therefore the adsorption process can takes place. The combination of membrane and activated carbon can help in removing the heavy metals. Presently, activated carbon is the most frequently used adsorbent and proven to have the capability to remove pollutants from contaminated water as it has high surface area, great adsorption capacity, fast kinetics and effective regeneration (Febrianto et al., 2009) . Activated carbon is a good adsorbent for copper and lead ions, thus, it is selected as the additive to the membrane (Imamoglu & Tekir, 2008).

On the other hand, the flat sheet membrane used for this project is made from polysulfone. Membrane is semi permeable layer between two different phases and it controls the movement between those phases. The liquid will pass through the membrane while at the same time it traps the suspended solids and other substances (Padaki et al., 2015). The concept of membrane is illustrated in Figure 1.1. The membrane is produced by polysulfone, N-methyl-2-pyrorolidone as solvent and activated carbon, polyethyleneimine and silver nitrate as additives. The membrane is fabricated by using phase inversion method in which this method will control the polymer transformation from liquid to solid phase. For this project, the transformation will be accomplished by applying immersion precipitation technique. Immersion precipitation technique is a method where the polymer solution is immersed in a non-solvent coagulation bath in which water bath is usually used (Lalia, Kochkodan, Hashaikeh, & Hilal, 2013).

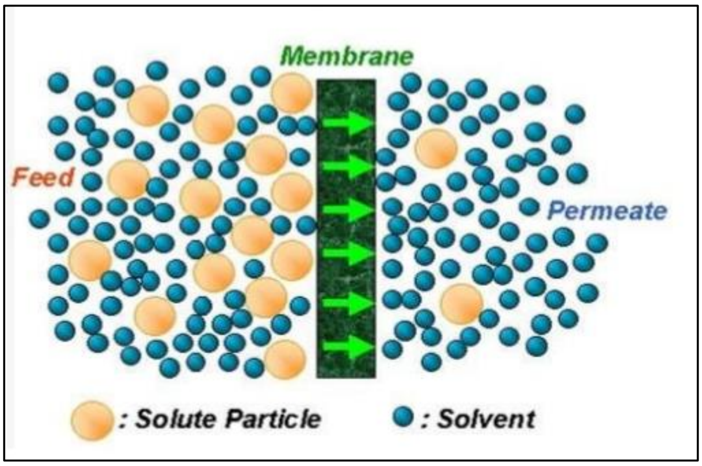

Figure 1.1: Concept of membrane (Khawwam, 2016)

According to Foo & Hameed (2010), an adsorption isotherms is the curve explaining the phenomenon governing the retention of a substance from the aqueous porous media or aquatic environment to a solid state with the condition of constant temperature and pH. Adsorption isotherms is a study on the interaction of adsorbate and adsorbents and equilibrium condition is initiated between adsorbed metal ions on the desired adsorbent and the remaining metal ions in the solution during the surface adsorption (Sekar et al., 2004). Meanwhile, the adsorption equilibrium is a functional expression that correlates the adsorbed amount and the remaining amount in the solution which is implemented when an adsorbate has been reacted with the adsorbent for certain time and the condition of the adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration (Foo & Hameed, 2010). There are many types of isotherm adsorption models including Langmuir, Freundlich, Temkin, Brunauer-Emmett-Teller, Redlich-Peterson and several more. However, in many treatment fields, adsorption by activated carbon is represented by isotherm adsorption which is either Langmuir isotherm or Freundlich isotherm (Reed & Matsumoto, 1993). Both of the isotherm models and also another isotherm model which is Temkin isotherm model are used to verify the adsorption performance of the adsorbent.

Langmuir isotherm is a gas-solid phase adsorption onto activated carbon which is applied to determine and compare the performance of different bio-sorbents. Langmuir isotherm model presumes that the highest adsorption occur to a saturated monolayer of adsorbate molecules on the adsorbent surface where the adsorption energy is remain constant and there is no movement of adsorbate in the plane of the surface (Abdel Salam, Reiad, & ElShafei, 2011). According to Foo & Hameed (2010), for this model, the adsorption process can only happen at fixed and identical number of definite localized sites which are identical and equivalent and there is no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. In term of its derivation, Langmuir isotherm describes the homogeneous adsorption and based on the theory, this model refers to the fast reduction of the intermolecular attractive forces to the rise of distance (Foo & Hameed, 2010).

Freundlich isotherm is the derivation that refers to the non-ideal and reversible adsorption but not only limited to the monolayer adsorption. Based on Abdel Salam et al. (2011), Freundlich isotherm model encompassing the surface. Unlike Langmuir isotherm, this model can be utilized to multilayer adsorption, with inconsistent distribution of adsorption heat and affinities over the heterogeneous surface. At different solution concentrations, this model proves that the ratio of the adsorbate onto an adsorbent with known mass to the solute would not be constant. The amount adsorbate is the total amount of the adsorption on all sites with the stronger engaging sites must be occupied first until adsorption energy are exponentially reduced after the process is complete. Heterogeneous systems such as organic compounds or highly interactive species onto activated carbon and molecular sieves being widely applied for this isotherm model. However, at present, this type of isotherm is criticized due to its limitation of lacking a fundamental thermodynamics basis and at vanishing concentration, it fails to approach the Henry's law (Foo & Hameed, 2010).

Temkin isotherm model was originally develop to describe the adsorption of hydrogen onto platinum electrodes within the acidic solution (Febrianto et al., 2009; Foo & Hameed, 2010). The derivation of Temkin equation is proposed according to the assumption that the reduction of the sorption heat in terms of temperature is linear rather than logarithm. According to Febrianto et al. (2009), this model is based on the prediction of gas phase equilibria. In contrast, this model is not appropriate in representing the equilibria data for the adsorption of heavy metals as it is a liquid phase adsorption which is more complex than gas phase adsorption. Thus, the complex phenomenon involved in liquid phase adsorption are not valid for this equation since the Temkin is derived based on a simple assumption.

1.2 Problem Statement

Pollution caused by heavy metal ions that disposed to the environment is a serious problem as their toxic may affect human health and living organism. Heavy metal contamination in water and wastewater were effect from industrial wastes such as metal plating, mining, tanneries and many more (Imamoglu & Tekir, 2008). There are numerous heavy metals that are known to be harmful for human beings and ecological environment such as copper, lead, zinc, chromium and nickel. Since lead is mostly used material, thus many possible pollution may occur due to lead. Therefore, for this project, lead is selected to be treated in order to reduce the amount of lead exposed to the environment. Lead is known as poisonous compound which acute lead poisoning may affect the gastrointestinal tract and nervous system (Imamoglu & Tekir, 2008). Besides, constant exposure to lead causes learning disabilities in children, damage to organs such as the liver, kidneys and heart, and immune system disorders (Cechinel et al., 2013). The lead exist in the wastewater of many industrial processes such as the production of paint coatings, dyes, glass and batteries are possibly toxic to humans and aquatic environment (Cechinel et al., 2013).

Recently, the conventional membrane is majorly developed for filtration process. There is technology that uses membrane for both filtration and adsorption processes but it requires high cost as it is the combination of nanotechnology. Meanwhile, adsorption process usually used low cost adsorbent to adsorb the heavy metals. The adsorption process presently includes isotherm adsorption used powdered adsorbent such as activated carbon that should be filtered first which is not convenient. Therefore, new method which is more convenient, require less space and able to disinfect bacteria should be proposed. Usually, the combination of various treatment processes can provide high quality treated effluent (Yu, Zhang, Shukla, Shukla, & Dorris, 2000). Thus, the membrane that can do both filtration and adsorption processes should be produced so the process of removing heavy metals are more convenient and the function of membrane is not limited for filtration process only. Hybrid adsorbent which is the combination of membrane and activated carbon will be used to undergo the adsorption process for heavy metal removal. The adsorption process will be verified by using isotherm adsorption models which for this project the models that will be emphasized are Temkin model, Langmuir model and Freundlich model.

1.3 Research Gap

This project is conducted to study the adsorption process of heavy metals by using membrane incorporated with activated carbon. Hybrid adsorbent which is made from the combination of polymer membrane and activated carbon will be produce to adsorb the selected heavy metal. This adsorption process will be proved by using isotherm adsorption model which is either Langmuir isotherm, Freundlich isotherm or Temkin isotherm. The combination of activated carbon and membrane's performance to act effectively in adsorption of heavy metals will be investigated.

1.4 Aim and Objectives

The aim of this project is to prove that the adsorption of heavy metals can be done by using membrane incorporated with activated carbon and verified the process by using isotherm model. The objectives of this projects are:

i. To characterize the membrane by using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR)
ii. To study the adsorption isotherm of heavy metals by membrane with activated carbon
iii. To verify the adsorption process by using Langmuir isotherms, Freundlich isotherm and Temkin isotherm model

1.5 Scope of Study

i. Preparation of dope solution by using polysulfone (PSU) as base polymer, polyethyleneimine (PEI) as second polymer, N-Methyl-2-Pyrolidone (NMP) as solvent, activated carbon (AC) as adsorbent and silver nitrate ($AgNO_3$) as source of antibacterial agent
ii. Fabrication of composite membrane PSU/NMP/PEI/AC/$AgNO_3$ by applying immersion precipitation phase inversion method
iii. Characterize the membrane by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR)
iv. Applied Langmuir, Freundlich and Temkin isotherm model to prove the adsorption of heavy metals by membrane with activated carbon by conducting batch experiment
v. Verify the adsorption process by applying the Langmuir equation ($q_e = \frac{Q_o b C_e}{1+bC_e}$), Freundlich equation ($q_e = K_F C_e^{\frac{1}{n}}$)and Temkin equation ($\mathrm{q_e = \frac{RT}{b_T} lnA_T C_e}$)