# ADSORPTION AND EQUILIBRIUM CHARACTERISTICS OF CADMIUM AND NICKEL ON PALM OIL FUEL ASH (NON-TREATED AND TREATED WITH NITRIC ACID)

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THIS DISSERTATION IS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF BACHELOR OF SCIENCE OF SCIENCE WITH HONOURS



INDUSTRIAL CHEMISTRY PROGRAMME
SCHOOL OF SCIENCE AND TECHNOOGY
UNIVERSITY MALAYSIA SABAH

2010

PUMS99:1

# UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN STATUS TESIS@

JUDUL: ADSOPTION AND EQUILIBRIUM CHARACTERISTICS OF CADMIUM AND NICKEL ON PALM OIL FUEL ASH (NON-TREATED AND TREATED WITH NITRIC ACID

IJAZAH: SARJANA MUDA SAINS (KEPUJIAN)

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# ACKNOWLEDGEMENT

It is a great pleasure that I have now the opportunity to express my appreciation to everyone who had played important role in the development of this study. It is grateful that this research can be completed on time and undergone successfully.

First of all, I would like to express my thankfulness and gratitude to my supervisor, Dr. Sazmal Effendi bin Arshad for his valuable suggestions and encouragement. I appreciate his effort for guiding me and enriching my knowledge towards this study.

Special thank to all the lecturers in Industrial Chemistry Program in School of Science and Technology. All their useful advices, comments, suggestions and guidance are much appreciated.

Besides that, I would also like to thank to my family members and friends who are always giving me full support, understanding and constantly teaching me in this study.

I would like to thank to the library. Library has provided me much useful information, reference books and various sorts of journals. Regarding to these facilities, I was able to finish this study easily.

Lastly, but not the least, I would like to appreciate to the persons who are contributing in helping me through this project. Thank you.

**ABSTRACT**

Palm oil fuel ash, POFA, an abundantly available throwaway waste from palm oil industry in Malaysia, has currently investigated to be an ideal adsorbent in the wastewater treatment processes. The experiment for the adsorption of Ni (II) and Cd (II) ions from aqueous solutions on non-treated and treated POFA was conducted to investigate the initial ions concentration (2-10 μg $mL^{-1}$), contact time (5-90 min) and binary components system. The equilibrium adsorption data were analyzed by using the Langmuir and Freundlich isotherms. Both isotherms were best fit to the experimental data for non-treated and treated POFA. The maximum adsorption capacity of Ni (II) and Cd (II) on treated POFA were 526.32 μg $g^{-1}$ and 769.23 μg $g^{-1}$ respectively which were higher than the adsorption of Ni (II) and Cd (II) on non-treated POFA which were 500.00 μg $g^{-1}$ and 714.29 μg $g^{-1}$ respectively. The experimental data were also tested in terms of adsorption kinetics by using pseudo-first order, pseudo-second order and intra-particle diffusion. The adsorption of Ni (II) and Cd (II) ions on non-treated and treated POFA followed well to the pseudo-second order kinetic model. The amount of adsorption for Ni (II) and Cd (II) on treated POFA was always higher than non-treated POFA. The adsorption capacity of Cd (II) was also higher than Ni (II) for the binary components system and was in agreement with the single component adsorption data. The binary components system was generally found to be antagonistic, which stated that the amount of adsorption in binary components system was lower than the amount of adsorption in single component system. Based on all the results, POFA could be used as an alternative low cost adsorbent to effectively adsorb Ni (II) and Cd (II) ions from wastewater.

PROSES JERAPAN DAN CIRI-CIRI KESEIMBANGAN KADMIUM DAN NIKEL OLEH ABU BAHAN KELAPA SAWIT (DIRAWAT DAN TIDAK DIRAWAT DENGAN ASID NITRIK).


## ABSTRAK

Abu bahan kelapa sawit (POFA) banyak terdapat dalam sisa-sisa buangan dari industri kelapa sawit di Malaysia, kini diselidik untuk menjadi bahan jerapan yang berkesan dalam rawatan air buangan. Eksperimen bagi process jerapan logam nikel dan kadmium pada POFA yang telah dirawat dan tidak dirawat dengan asid nitrik dijalankan untuk mengkaji kepekatan awal ion logam (2-10 $\mu g\ mL^{-1}$), masa tindak balas (5-90 min) dan sistem binari. Data keseimbangan jerapan dianalisis oleh isoterma Langmuir dan Freundlich. Kedua-dua jenis isoterma ini sesuai untuk menjelaskan data eksperimen bagi POFA yang telah dirawat dan tidak dirawat dengan asid nitrik. Kapasiti jerapan maksimum bagi logam nikel dan kadmium pada POFA yang dirawat dengan asid nitrik ialah 526.32 $\mu g\ g^{-1}$ dan 769.23 $\mu g\ g^{-1}$ adalah lebih tinggi daripada jerapan logam nikel dan kadmium pada POFA yang tidak dirawat dengan asid nitrik, iaitu masing-masing ialah 500.00 $\mu g\ g^{-1}$ dan 714.29 $\mu g\ g^{-1}$. Data eksperimen ini juga digunakan untuk menganalisis kinetik jerapan, iaitu 'pseudo-first order', 'pseudo-second order' dan 'intra-particle diffusion'. Proses jerapan logam nikel dan kadmium pada kedua-dua jenis POFA mematuhi kinetic jerapan 'pseudo-second order'. Jumlah jerapan bagi nikel dan kadmium pada POFA yang telah dirawat dengan asid nitrik selalunya lebih tinggi daripada jerapan logam nikel dan kadmium pada POFA yang tidak dirawat oleh asid nitric. Kapasiti jerapan bagi kadmium adalah lebih tinggi daripada jerapn nikel pada kedua-dua jenis POFA dalam sistem binari dan ini juga disetujui dalam sistem tunggal. Sistem binari dalam eksperimen ini menunjukkan bentuk antagonis, iaitu jumlah jerapan pada sistem binari adalah lebih rendah daripada sistem tunggal. Kesimpulannya, POFA boleh digunakan sebagai bahan penjerap yang berkesan untuk menjerap logam nikel and kadmium dalam rawatan air buangan.

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| | |
|---|---|
| $[Cd(NO_3)_2.4H_2O]$ | Cadmium nitrate tetrahydrate |
| $[Ni(NO_3)_2.6H_2O]$ | Nickel nitrate hexahydrate |
| % | Percentage |
| *b* | Adsorption energy constant of Langmuir adsorption isotherm (mL $\mu g^{-1}$) |
| $Cd^{2+}$ | Cadmium ion |
| $C_e$ | Equilibrium liquid phase concentration ($\mu g$ $mL^{-1}$) |
| $C_f$ | Final liquid phase concentration ($\mu g$ $mL^{-1}$) |
| $C_i$ | Initial liquid phase concentration ($\mu g$ $mL^{-1}$) |
| FAAS | Flame Atomic Absorption Spectrophotometry |
| $k_1$ | Rate constant of pseudo-first order adsorption (1/min) |
| $k_2$ | Rate constant of pseudo-second order adsorption (g / g min) |
| $k_f$ | Freundlich isotherm constant related to adsorption intensity (mL $g^{-1}$) |
| $k_{id}$ | Intra-particle diffusion rate constant ($\mu g$ $g^{-1}$ $min^{-1/2}$) |
| *n* | Freundlich adsorption constant (mL $\mu g^{-1}$) |
| $Ni^{2+}$ | Nickel ion |
| POFA | Palm Oil Fuel Ash |
| $q_e$ | Equilibrium solid phase adsorbate concentration ($\mu g$ $g^{-1}$) |
| $q_{max}$ | Maximum adsorption capacity ($\mu g$ $g^{-1}$) |
| $q_t$ | Amount of adsorption at time, t ($\mu g$ $g^{-1}$) |
| $R^2$ | Correlation coefficient |
| $R_L$ | Dimensionless separation factor |

| | |
|---|---|
| $t$ | Contact time (min) |
| V | Volume of solution (mL) |
| w | Mass of adsorbent (g) |

# CHAPTER 1

# INTRODUCTION

## 1.1 Context and Relevance of Study

Recently, there is an increasing concern about the contamination of heavy metals in wastewaters. This is not threatening the environment, but also the life form due to their non-biodegradable characteristics and bioaccumulation in the food chain and persistence (Khesami and Capart, 2005). This has become one of the important environmental issues.

Heavy metal pollution in water normally generated from many types of industry like electroplating, metal plating, batteries, mining, pigments, stabilizers, alloy industries and sewage sludge (Patnukao *et. al.*, 2008). These pollutants include copper, lead, nickel, cadmium and so on. The increased use of metals and chemicals in these industries has resulted in the generation of large amounts of polluted aqueous effluents which contain high levels of heavy metals and pose environmental disposal problems for plants, animals and human beings (Gok *et. al.*, 2008). Therefore, the treatment of wastewaters to remove heavy metals from wastewaters is necessary.

A wide range of treatment methods have been applied for the removal of heavy metals from industrial waste streams. These methods include chemical precipitation, coagulation, ion-exchange, solvent extraction, membrane processes, reverse osmosis, ultrafiltration, adsorption and electrochemical deposition (Gok *et. al.*, 2008). However, most of these methods may be ineffective, expensive, generation of secondary pollution and ineffectiveness for low metal concentration (Bhattacharyya and Gupta, 2006). Among these methods, adsorption is the most effective, simply and widely used because of its cost effectiveness (Boujelben *et. al.*, 2009). Adsorption is the most promising techniques for the metal removal and recovery from wastewaters (Chu and Hashim, 2002).

In recent years, numerous low cost materials have been proposed as potential replacements for the effective but expensive synthetic sorbents such as activated carbon (Bailey *et. al.*, 1999). Activated carbon is expensive due to the use of non-renewable and relatively expensive starting material such s coal, which is unjustified in pollution control applications (Martin *et. al.*, 2003). The adsorbents usually used for the metal removal in water streams are anion exchange resins, clay minerals such as bentonite and zeolite because of their high specific area and low cost (Gao *et. al.*, 2009). Fly ash has been extensively investigated for its ability to remove metals ions from aqueous solutions. Most of these studied focused on the fly ash which derived from coal-fired power plants (Kapoor and Viraraghavan, 1992, 1996; Weng and Huang, 1994; Singer and Berkgaut, 1995; Apak *et al.*, 1998, Dasmahaptra *et al.*, 1998; Gupta and Torres, 1998; Ricou *et al.*, 1998, 1999; Ricou-Hoeffer *et al.*, 2000).

Malaysia is the world's largest producer of palm oil which produces a large amount of solid waste such as palm shells and palm fiber. The palm oil fuel ash is a by-product in palm oil mill after the combustion of palm fiber and palm shell as boiler fuel (Tangchirapat *et. al.*, 2009). POFA is still considered as a nuisance to the environment and disposed without being put for any other use as compared to other types of palm oil by-products. Since the production of palm oil is continuous, therefore, more ashes will be produced and failure to allocate this by-product will create severe environmental problems (Abdullah *et. al.*, 2006).

However, POFA has currently suggested being an ideal adsorbent in the wastewater treatment processes and as air purifiers in cleaning of atmosphere contaminations (Dahlan *et. al.*, 2007). There are two advantages of using POFA, first, huge loads of oil palm waste could be partly reduce by converted into an useful, value-added adsorbents, and second, become a low-cost adsorbent. If developed, may overcome the wastewaters and air pollution at a lower cost, solving part of global agricultural refuse and wastewater treatment problem (Ahmad *et. al.*, 2007).

## 1.2 Objectives

The objectives of this study are:

1. To investigate the adsorption and equilibrium characteristics of cadmium and nickel based on POFA as an adsorbent.
2. To compare adsorption equilibrium and kinetics of cadmium and nickel by treated and non-treated POFA.

## 1.3 Scope of Study

The scope of this study is to study the utilization of POFA as an adsorbent to remove cadmium and nickel from aqueous solutions. The adsorption of cadmium and nickel was determined at different reaction times, initial concentrations of cadmium and nickel and the uptake of cadmium and nickel by POFA in binary system. Then, the final concentrations of cadmium and nickel were analyzed by using atomic adsorption spectrometry (AAS). The metal uptake of cadmium and nickel on POFA was studied for its mechanism, equilibrium and kinetic.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Heavy Metals

Heavy metals are metallic chemical elements that have a relatively high density, high atomic weight and are toxic or poisonous at low concentrations. Examples of heavy metals include mercury, nickel, cadmium, arsenic, chromium, thallium, lead and so on.

Heavy metals pollution by industrial activities and technological development has a greater side effect to the environment and public health because of its toxicity, non-biodegradability and bioaccumulation (Bahadir *et. al.*, 2007; Pérez-Marin *et. al.*, 2007; Reddad *et. al.*, 2003). Besides the mining and metal-related industries, there are numerous sources that discharge heavy metal-laden effluents, such as the tanning, battery, glassware, ceramics, electroplating, paints and photographic industries (Bhatnagar and Minocha, 2009).

Actually, many metals are important for human life in trace quantities, they enter our bodies through food, drinking water and air, but become toxic if their concentration increases above a certain minimum level. Heavy metals may accumulate in microorganisms, aquatic flora and fauna, which in turn may enter into the human food chain and bring into health problems (Orozco *et. al.*, 2008).

### 2.1.1 Heavy Metal in Water

Heavy metals can enter water supply through industrial activities, consumer wastes or from acidic rain which breaks down soils and then releases heavy metals into streams, lakes, rivers and groundwater.

Heavy metal contaminations in water normally because of dischargeable of heavy metal which are often generated from many types of industry, such as electroplating, metal plating, batteries, mining, pigments, stabilizers, alloy industries and sewage sludge into water streams (Patnukao *et. al*, 2008). These contaminants include copper, lead, nickel, cadmium and so on. The increase use of metals and chemicals in these industries has resulted in the generation of large amounts of polluted aqueous effluents which contain high levels of heavy metals and pose environmental disposal problems for plants, animals and human beings (Gok *et. al*, 2008). Natural weathering processes, waste emissions, atmospheric depositions and anthropogenic activities also contribute to the heavy metals pollution in water bodies (Gok *et. al*, 2008).

### 2.1.2 Sources of Heavy Metal

The sources of heavy metal ions are diverse and specific to each element. Most heavy metals are generated from industrial processes and mining activities (Ozdemir and Yapar, 2009). These industrial processes include electroplating, metal-processing, paint, plastics alloy, batteries, ammunition and the ceramic glass industries and so on (Guo *et. al.*, 2009). Besides that, some heavy metals are found in our daily use, such as aluminum is mostly encountered in kitchen utensils whereas nickel is found in cigarette and plant foods (Kasprzak *et. al.*, 2003). Moreover, Cadmium originates mainly from cigarette smoke (Waisberg *et.al.*, 2003), air pollution, batteries and Cd-containing polishing agent (Gunnar F. Nordberg, 2009).

### 2.1.3 Toxicity of Heavy Metal

Even at a low concentration level, heavy metal ions can cause serious health problems and in extreme cases, death. Toxic metals at trace levels contamination of soil and

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