



The Effect of Adsorbent Mass on the Removal of Heavy Metal Ion Using Domestic Waste

By

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Dissertation submitted in partial fulfillment of the requirements for the Bachelor of Engineering (Hons) (Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the Chemical Engineering Programme Universiti Teknologi PETRONAS in partial fulfilment of the requirement for the BACHELOR OF ENGINEERING (Hons) (CHEMICAL ENGINEERING)

Approved by,

(Dr. Ku Zilati Binti Ku Shaari)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2009



CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NOOR FAEZAH BINTI RAMLY



ABSTRACT

This paper presents "The Effect of Solution pH and Adsorbent Mass on the Removal of Heavy Metal Ion Using Domestic Waste" which aims to study the capability of cockle shell and burned palm as alternatives adsorbents to expensive activated carbon in removing cadmium and nickel at different solution pH and adsorbent mass. Cadmium and nickel are the major wastes in battery industry and have significant effect to surroundings. In view of the human health impacts, cadmium exposure can affect the fertility and lead to kidney damage, whereas nickel has an effect on nerve system. Also, both heavy metals are known to be carcinogenic. Cockle shell and burned palm trunk potential in removing those heavy metals are studied as both can be obtained cheap from byproduct and wastes in seafood and palm plantation industry since they have no other usage. This also can be a way to utilize and minimize domestic waste which results unsoiled environment. Adsorption is a pH-dependent process. Hypothetically, the adsorption rate will increase in base condition. The pH of the solution affects the charge on the surface of the adsorbents and concentration of hydrogen ions, the strong competing ions. Mass of adsorbent in the other hand, affect the availability of larger surface area and adsorption sites. This paper also discusses the equilibria and kinetic aspects of biosorption. The Langmuir and Freundlich isotherms are used for biosorption equilibria representation, and pseudo-first and second order for kinetic studies.



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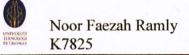


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1. INTRODUCTION

1.1. Background of Study

Heavy metals are widely used in industries for battery manufacturing, printing and pigment, metal plating and finishing, ammunition, soldering material, ceramic and glass industries [1]. Improper disposal of these is the cause for environmental pollution problems, ecosystem damage and human health deteriorate. Some of the major heavy metals are essential to sustain life, but considered toxic when critical dosages are exceed, and later led to fatality. Nickel is known to be carcinogenic [2, 3]. Besides, nickel affects nervous system. Heavy metals penetrate in human system via several ways, 1) high natural concentration of metals in food and water, 2) smelting and fume inhalation, 3) intact or abraded skin [4].

Various technologies have been developed over the years to remove toxic metal ions from water, such as filtration, chemical precipitation, ion exchange adsorption, electrodeposition, evaporation, cementation electrolysis, reverse osmosis, membrane systems and ion exchange adsorption [5, 6]. Despite the availability of numerous techniques for the treatment of effluents with heavy metals, adsorption is constantly viewed as highly effective technique, especially in low metal concentration solutions. This study will be focusing on heavy metal ions adsorption using domestic wastes. Common adsorption practice in industry is by utilized expensive activated carbon. Domestic wastes, in this study are burned palm trunk and cockle shell are hoped to be cheaper substitutes for the costly adsorbent. Based upon the metal binding capacities of various biological materials, these adsorbents can separate heavy metals from wastewater because of their constituents, which are mainly proteins, carbohydrates and phenolic compounds, since they contain functional groups such as carboxylates, hydroxyls and amines, which are able to attach to the metal ions. Besides, it is a way to utilize the domestic waste rather than just dispose it.



1.2. Problem Statement

1.2.1. Problem Identification

Heavy metal does not have a rigorous scientific basis or chemical definition. But most of these elements have specific gravities greater than five, with major exception to this rule. United States Environment Protection Agency's (USEPA's) refers this group as "toxic elements" and enlist as priority pollutants, for instance, nickel, mercury, cadmium, copper, selenium, arsenic and etc. This study is focusing on removal of nickel from aqueous solution. Both of these heavy metals are widely used in industry, especially in batteries industry. If not properly dispose, it will affects creature and environment. Their presence in the wastewater of several industrial processes has brought about more environment concern due to their toxicity even at low concentrations. In view of the human health impacts, each metal imparts different effects and symptoms. The presence of nickel exceeding its critical level might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis.

1.2.2 Significant of the Project

Commonly, activated carbon is used to remove these heavy metals. However, the high price of activated carbon is regarded as the major obstacle for industrial large scale application. From an economic point of view, it is infeasible to utilize activated carbon for commercial wastewater treatment. To that end, the focus of heavy metal adsorption studies has been altered toward natural materials that are available in vast amounts, as well as certain waste products from industrial and agricultural operations, or better known as biosorption. This research is mainly to uncover cockle shell and burned palm trunk potential as alternative adsorbents in removing nickel in aqueous solution. Both can be obtained cheap from byproduct and wastes in seafood and palm plantation industry since they have no other usage. This also can be a way to utilize and minimize domestic waste which results unsoiled environment.

1.3. Objective and Scope of Study

The objectives of this research are;

- To study cockle shell and burned palm trunk potential as alternative adsorbents
- To study the effect of adsorbents mass on the adsorption rate.

1.4. The Relevancy of the Project

Nickel is the major wastes in battery industry and has significant effect to surroundings. Thus, it is crucial to remove those heavy metals before disposing it. Burned palm trunk is chosen as it is pre-assume to have almost similar activated carbon capability and trait. Based on studies on crab shell for the removal of heavy metals from aqueous solution done by H. K. An in 2000, heavy metal ions removal is favored by crab shell a lot better than activated carbon. The study also indicates heavy metals selectivity, with lead and chromium are being removed in preference to cadmium and copper. Therefore, cockle shell is selected as another potential adsorbent, with the hypothesis of cockle shell has the same functional group as crab shell. Moreover, these potential adsorbents are also widely available, cheap and environmentally safe. Heavy metals removal via adsorption is pH-dependent. Generally, heavy metals ions removals is increase with increasing of pH, but metal ions may be hydrated with multiple hydroxyl groups and the solubility may be lower in base condition. Nonetheless, adsorbent mass which is the other parameter studied is affecting the availability of surface area and adsorption sites. The aim of this research is to find the optimum condition for the adsorption using domestic waste to take place.



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1.5. Feasibility of the Project within the Scope and Time Frame

Basically, this study is divided into three stages, which are as follows,

- 1. Research
- 2. Adsorbent preparation
- 3. Adsorbent mass experiment

Firstly, for the first six months, the report about previous works were gathered to be analyzed for information regarding preceding study on domestic waste utilization for biosorption, parameter focused on and a means to combine the effect of the operating parameters. Then, in experimental stage, the adsorbents were prepared before tested for the mass adsorbent effect.

2. LITERATURE REVIEW

2.1 Heavy Metals

2.1.1. Nickel

Nickel (Ni) is one of only four elements that are magnetic at or near room temperature, or better known as ferromagnetic. In early years, nickel's ore is mistaken for a copper mineral, until 1751. It occurs most often in combination with sulfur, iron and arsenic. Nickel is a very reactive element, but is slow to react in air at normal temperature and pressure due to the formation of a protective oxide surface. Due to its permanence in air and its slow rate of oxidation, it is used in coins, for plating metals, for chemical apparatus and in certain alloys. Table 2.2 shows nickel physical properties.

Chemical symbol	Ni
Phase	Solid
Appearance	Lustrous, metallic and silvery with a gold
	tinge
Characteristics	Hard and ductile
Melting point	1453 °C
Boiling point	2732 °C
Heat of fusion	17.48 kJ.mol ⁻¹
Heat of vaporization	377.5 kJ.mol ⁻¹
Specific heat capacity	(25 °C) 26.07 J.mol ⁻¹ K ⁻¹
Atomic number	28
Atomic weight	58.69
Density	(liquid density at melting point) 8.91
	g/cm ³

Table 2.	1: Nickel	physical	properties
----------	-----------	----------	------------

Nickel is used in many industrial and consumer products, including rechargeable battery, stainless steel, alloys, magnets and coinage. In battery industry, nickel is utilized for nickel cadmium (NiCd) and nickel metal hydride (NiMH) battery. Rechargeable battery also best known as secondary cells used as automobile starters, portable consumer devices such as handphone and laptop, light vehicles and light tools. It is also used for plating and as green tint in glass.

Nickel can enter one's body when it is inhaled, eaten, drink or in contact with skin. However, it is depend on the dosage, duration and how been exposed for nickel to be harmful. Age, gender, diet, family traits, lifestyle and health state also affect the consequence of the metal. Certain nickel compound fume and dust is believed to be carcinogenic. However, the most common harmful health effect of nickel in human is an allergic reaction. Approximately 10-20% of the population is sensitive to nickel. A person can become sensitive to nickel when jewelry or other items containing nickel are in direct contact and prolonged contact with the skin and dermatitis may develop. More women are sensitive to nickel than men as them is exposed to nickel greater through jewelry. The most serious harmful health effects from nickel exposure are chronic bronchitis, reduced lung function, lung cancer and nasal sinus, result from inhaling the dust containing nickel sulfide.

2.2. Adsorbents

There are three adsorbents selected throughout this project to study its feasibility in industrial usage, which are,

- 1. Activated carbon
- 2. Burned palm trunk
- 3. Cockle shell

Activated carbon is the usual adsorbent in removing organic contaminants from wastewater streams with great success due to its large surface area, micro-porous structure, high adsorption capacity and etc. however, its use is limited because of its high cost. This has led to search for cheaper substitutes [9]. In other words, this study's objective is to investigate the potential of using burned palm trunk and cockle shell as low-cost adsorbents for the removal of nickel from aqueous solutions. For that reason, it been selected as control element to compare with the other two adsorbents.

The last two adsorbents are generalized as biosorption. Biosorption is a term used to describe the removal of heavy metals using a passive binding process with nonliving microorganisms including bacteria, fungi and yeasts [10] and other biomass types that are capable of efficiently collecting heavy metals. Obviously, some of the advantages biosorption has over conventional treatment methods include low cost, high efficiency for dilute concentration solutions, a minimal amount of chemical and/or biological sludge, no additional nutrients required and the possibility of biosorbent regeneration and metal recovery [11]. The sorption of heavy metal onto these biomaterials is

attributed to their constituents, which are mainly proteins, carbohydrates and phenolic compound, since they contain functional groups such as carboxylates, hydroxyls and amines, which are able to attach to the metal ions [12].

2.2.1. Activated Carbon

Activated carbons, both powdered and granular, are made from wide variety of carbonaceous starting materials, like coals, wood, sawdust, coconut shells and etc. They are manufactured in such a way that they have a tremendous network of pores inside, and the total surface area inside such carbons is typically 500 to 1500 m²/g. It is this extensive surface on which adsorption of organics can occur. Adsorption amounts up to as high as 0.30 g organic/g carbon are not usual. Experimentally, activated carbons have been proven capable of adsorbing more than their own weight, 3000 m²/g in fact and figure [13].

While most of carbonaceous substances can be converted into activated carbon, the properties of the carbon will depend significantly on the nature of the starting material. This is especially the case with regard to the hardness of the final products, for instances, coconut shells yield a strong, dense carbon which resist mechanical abrasion well [13].

There are processes for making activated carbons to get those special characteristics. Commonly applied are pyrolysis or also known as carbonization and controlled oxidation.

The pyrolysis step involves heating the source material to temperature ranging between 600 and 900 °C in the absence of air. The addition of metal chlorides to the starting material has been found to promote the development of pores during pyrolysis. For instances, in Europe, the sawdust or pulverized peat is mixed with a concentrated zinc chloride solution, dried and carbonized in kiln at 600 to 700 °C. A subsequent washing



step with dilute acid or simply water is employed to remove the zinc chloride from the product. The process will stop here if only large pores are desired in the carbon, as in case of those used for decolorizing sugars, where the color bodies to be adsorbed are fairly large molecules which can penetrate only into large pores [13].

The next step is carbon activation with oxidizing gases. The basic characteristics of a carbon are established during the pyrolysis, and the ensuing oxidation step must be designed to complement the pyrolysis step. The various changes which occur do not all take places at the same rate. Time allowed for activation is a very important variable that affect the sizes of the pores developed and the ability of a carbon to adsorb different materials. As time goes on, the carbon pores will become larger. Oxidation is usually performed using steam, although air is sometimes chosen. Temperatures are normally in the range of 600 to 900 °C. During this step, the oxidizing gas increasingly erodes the internal surfaces of the carbon, develops an extensive and fine network of pores in the carbon, and changes the atom lying on the surfaces to specific chemical forms which may have selective adsorption capabilities. The reaction which occur during activation are,

 $C + H_2 O \rightarrow H_2 + CO$ $C + CO_2 \rightarrow 2CO$ $C + \frac{1}{2}O_2 \rightarrow CO$

These reaction cause solid carbon (C) to be converted to gaseous species, thereby creating pores in the carbon [13].

Depending on the nature of the partial oxidation reactions which occur during the activation of a carbon, either of two forms of carbon may result. "H-type" carbons are produced under normal activation conditions, which are high temperature (>750 °C) and exposed to air at room temperature after that. "L-type" carbons in the hand are result



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from activating the carbons at low temperature (200 to 400 °C) in air. The carbons produced by most manufacturers are usually of the H-type. H-type carbons are hydrophobic and take on a positive charge when immersed in water, by adsorbing H⁺ ions, thus making the water alkaline. H-type carbons have basic surface oxides predominate with lactones, quinines, phenolic hydroxyls and carboxylates as surface functional groups [14]. Differ from H-type carbons, L-type carbons are hydrophilic and take on a negative charge when immersed in water, by adsorbing OH⁻ ions, thus making the water acidic. These carbons are acidic oxides predominate and have carboxyl, phenolic hydroxyl, carbonyl (quinine type), carboxylic acid, anhydride, lactone and cyclic peroxide groups as its surface functional groups [15]. It is known that the adsorption of organic compounds can be affected by the nature and amount of surface oxide groups. For example, phenol forms strong donor-acceptor complexes with oxygen groups, and thus its adsorption occurs by a donor-acceptor complex mechanism involving carbonyl oxygens of the carbon surface acting as the electron donor and the aromatic ring of the phenol acting as the acceptor. After the carbonyl oxygen sites are fully utilized, further adsorption can occur by complexation of the phenol with the graphitic rings of the carbon basal planes [16].

2.2.2. Burned Palm Trunk

Palm or *Palmae* or *Panamea* or also known by the name *Palmaceae* is widely exist in the tropics. Over two-thirds of palms live in tropical forests, where some species grow tall enough to form part of the canopy and other shorter palms adapted to shade form part of the understory. In Malaysia, palm is grown for its oil and other by-products. Burned palm trunk is chose because it is available in large quantities at one location, in this case is in Perak, environmentally safe, low economic value and less useful in alternative products. There is a huge palm plantation along Tronoh-Manjung road which belong to Sime Darby and the old ones are burned down for quality control purpose. These agricultural wastes can be utilized for more significant role, as alternative adsorbent in real wastewater treatment plant.

Burned palm trunk can be define as agricultural by-products which mostly composed of lignin and cellulose, as well as other polar functional group-containing compounds, which include alcohols, aldehydes, ketones, carboxylates, phenols and ethers. These groups are able to bind heavy metals through replacement of hydrogen ions with metal ions in solution or by donation of an electron pair from these groups to form complexes with metal ions in solution [17].

2.2.3. Cockle Shell

Cockle is the common name for a group of mostly small, edible, saltwater clams, marine bivalve mollusks in the family *Cardiidae*. Various species of cockles live in sandy sheltered beaches throughout the world [18]. Same case with burned palm trunk, widespread seafood industry in Lumut makes cockle shell waste widely available. Other than that, the shell only contains protein, calcium carbonate (CaCO₃) and calcite, which are not harmful. But, the heavy metals exhibit higher affinities towards sulfhydryl groups in proteins [13] thus, it makes a suitable alternative adsorbent.

2.3. Parameter

This project mainly focuses on adsorbents mass effect on the adsorption rate.

2.3.1. Adsorbents Mass

The removal of metal ion was found to increase with an increase in adsorbent dosage from 1 to 25 g/L. increase in adsorption with increase in adsorbent dosage attributed to the availability of larger surface area and more adsorption sites. At very low adsorption concentration, the adsorbent surface becomes saturated with the metal ions and the



residual metal ions concentration in the solution is large. With an increase in adsorbent dosage, the metal ion removal increases. For adsorbent dosage of 2.5 g/L, the incremental metal ion removal becomes very low as the surface metal ion concentration and the solution metal ion concentration comes to equilibrium with each other. For higher adsorbent dosage of 5.0 g/L, the removal efficiency becomes almost constant [19]. When quantity of adsorbent and concentration of metal ion is increased, the uptake rises sharply. This is attributed to greater adsorbent surface or number of adsorbent sites [28].

2.4. Calculation

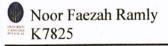
Removed heavy metal amounts per unit sorbent dry weight are calculated from heavy metal mass balance yield. The removed heavy metal amounts by sorbent is calculated as,

$$Q = \frac{V(C_0 - C_1)}{1000M}$$
[30]

Where,

Q: specific metal removal (mmol/g sorbent)
V: volume of metal solution (L)
C₀: initial concentration of metal in solution (mmol/L)
C₁: concentration of metal in solution (mmol/L)
M: dry weight of sorbent (g)

The initial heavy metal removal rate is measured by calculating the slope from Q versus time at t = 0. The definition of percent removal is a follows,



$$\% removal = \frac{C_0 - C_1}{C_0} \times 100$$

Where,

C₀: initial concentration of metal in solution (mmol/L) C₁: concentration of metal in solution (mmol/L)

2.4.1. Adsorption Isotherms

Adsorption isotherms represent the relationship between the mass of the solute adsorbed per unit mass of adsorbent, q_e and the solute concentration for the solution at equilibrium, C_e [19].

2.4.1.1. Langmuir Adsorption Isotherm

The Langmuir model is derived based on several assumptions, which are,

- 1. Monolayer adsorption onto a surface [19] / Adsorption on the surface is localized [31] / Each site can only accommodate one molecule or atom [31]
- Finite number of identical sites [19] / Every adsorption site is equivalent [28] / The surface is homogeneous [31]
- Ability of a particle to bind on the surface is independent of whether or not adjacent sites are occupied [28]

The model has the form as follows,

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e}$$

Where, q_e: amount adsorbed at equilibrium

13

[30]

[31]

 q_{max} : Langmuir constant, equal to adsorption capacity.

K_L: Langmuir sorption equilibrium constant

Ce: equilibrium concentration

Or

 $\frac{C_{eq}}{x_{m}^{\prime}} = \frac{1}{K_{1}K_{2}} + \frac{C_{eq}}{K_{2}}$

Where,

C_{eq}: equilibrium concentration of metal ion in solution
x: amount of metal ion adsorbed by a mass of adsorbent
m: mass of adsorbent
K₁: adsorption coefficient
K₂: limiting adsorptive capacity

Or

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}b} + \frac{C_e}{q_{\max}}$$
[19]

[28]

Where,

C_c: concentration of metal ion in solution at equilibrium (mg/L) q_c: amount adsorbed per g of the adsorbent at equilibrium (mg/g) q_{max}: maximum adsorption capacity (mg/g) b: Langmuir constant (L/mg)

Linear plot of C_e/q_e versus C_e is employed to determine the value of q_{max} (slope = $1/q_{max}$) and b (intercept = $1/q_{max}b$)

2.4.1.2. Freundlich Adsorption Isotherm

The limitations of Langmuir's theory are assumptions of unimolecular adsorption, and equivalence and independence sites. The previous study indicate that the Langmuir's isotherm is not able to describe adequately the adsorption behavior of metal ions uptake [2]. Alternatively, the Freundlich is an empirical equation is employed to predict adsorption equilibria data. The Freundlich equation can be written in the following form,

$$q = K_F C_e^{1/n} \tag{31}$$

Where,

K_F: Freundlich adsorption capacity n: heterogeneity of the system

The parameter n is usually greater than unity. A larger n values indicate that the system is more heterogeneous, which usually results in non-linearity of the adsorption isotherm.

Or

$$\frac{x}{m} = K_c C_{eq}^{1/N}$$

Where,

x: amount of metal ion adsorbed by a mass of adsorbent m: mass of adsorbent Kc: relative adsorptive capacity constant Ceq: equilibrium concentration of metal ion in solution

N: affinity constant.

28]

It also can be rewrite as

$$\log \frac{x}{m} = \log K_c + \frac{1}{N} \log C_{eq}$$

Or

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$
[19]

Where,

q_c: amount adsorbed per g of the adsorbent at equilibrium (mg/g)
K_f: measure of adsorption capacity (mg/g)
n: Freundlich constant, intensity of adsorption

C_e: concentration of metal ion in solution at equilibrium (mg/L)

The constants K_f (intercept = log K_f) and n (slope = 1/n) are calculated using Freundlich plots, log q_e versus log C_e . The values of n between 1 and 10 represent a favorable adsorption.

The conformity between experimental data and the model predicted values was expressed by correlation coefficient (r^2) and Chi-square test (χ^2). Correlation coefficient measure of how well two random variables are linearly related. More specifically, the value of r^2 indicates what proportion of the variation of y (the dependent variable) can be attributed to a linear relationship to x (the independent variable). The quantity r is given by,

$$r = \frac{N \sum x_i y_i - \sum x_i y_i}{(N \sum x_i^2 - \sum x_i \sum x_i)^{0.5} (N \sum y_i^2 - \sum y_i \sum y_i)^{0.5}}$$
[32]

[28]

Correlation coefficient value, r ²	Indication	
r=1	Perfectly linear with positive slope	
r=-1	Perfectly linear with negative slope	
r=0	Exactly horizontal	

Table 2.2: Correlation coefficient value indication

The Chi-square test (χ^2) can be expressed as,

$$\chi_{e}^{2} = \sum \frac{(q_{e} - q_{em})^{2}}{q_{em}}$$

If for instances, an experimental data better fitted to Langmuir than Freundlich adsorption isotherm, therefore the uptake of the metal ion is said to be preferably follows the heterolayer adsorption process [19].

2.4.2. Adsorption Kinetics Study

2.4.2.1. Pseudo-First-Order Model

Pseudo-first-order model can be express as,

$$\frac{q}{q_e} = 1 - \exp\left[k_A C_s + \frac{k_A}{k_s}\right]t$$
[19]

Where,

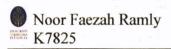
q: amount adsorbed per g of the adsorbent (mg/g)

qe: amount adsorbed per g of the adsorbent at equilibrium (mg/g)

k_A: adsorption rate constant

Cs: adsorbent concentration in solution (g/L)

t: time



The equation can be transformed to Lagergren equation [6] shown below,

$$\log(q_e - q) = \log q_e - \frac{K_{ad}t}{2.303}$$
[19]

Where,

 q_e : amount adsorbed per g of the adsorbent at equilibrium (mg/g), X_{Ae} q: amount adsorbed per g of the adsorbent (mg/g), X_A

$$K_{ad} = \left[\left(k_A C_s + \frac{k_A}{k_s} \right) \right] t$$

The Lagergren equation can be plot as $log(q_e-q)$ versus t.

2.4.2.2. Pseudo-Second-Order Model

The pseudo-second-order model is based on the assumption of chemisorption of the adsorbate on an adsorbent. The kinetic rate model can be represented as [33]

$$\frac{dq_i}{dt} = k(q - q_i)^2$$
^[19]

Where,

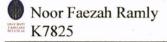
qt: amount adsorbed per g of adsorbent at time

t: time

k: pseudo-second-order rate constant of adsorption ((mg/g)min)

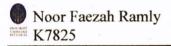
q: amount adsorbed per g of the adsorbent (mg/g)

Integrating the boundary conditions, qt=0 at time t=0,



$$\frac{t}{q_t} = \frac{1}{kq^2} + \frac{1}{q}t$$

This is a linear form equation for pseudo-second-order reaction. The constant k and q can be experimentally determined from t/q_t against t graph. From literature survey, it seems that the pseudo-second-order model is more common in comparison to the pseudo-first-order model. This suggests that the rate limiting step in heavy metal biosorption is chemisorption, which involves valence forces through the sharing or exchange of electrons between adsorbent and adsorbate, complexation, coordination and/or chelation, rather than physisorption [31]



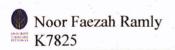
3. METHODOLOGY

3.1. Preparation of the Adsorbent

Activated carbon is commercially available for end-user, thus nothing have to do prior to experiment. In the case of cockle shell, it was cleaned by washing with water and final rinse with distilled water, and then dried. The dirt free cockle shell and burn up palm trunk were grinded and sieved to desired geometric mean particle size and stored at room temperature. The alternative adsorbents properties check, such as surface area, bulk density, moisture content, particle size distribution, structure and possible functional groups may be carried out if possible. Table 3.1 below show the list of equipments/techniques used to test out the adsorbents characteristics.

Characteristic	Equipment/techniques	
Structure	Scanning electron microscopic (SEM) micrograph	
Particle size distribution	Particle size distribution analyzer	
Possible functional groups	Fourier Transform Infrared (FTIR) Spectroscopy	
Possible compound percentage	X-Ray Powder Diffraction (XRD)	
Possible composition percentage	X-Ray Fluorescence (XRF)	
Surface area	Brunauer-Emmet-Teller (BET) nitrogen adsorption technique	
Bulk density	Specific gravity bottle	
Moisture content	Digital microprocessor-based moisture analyzer	

Table 3.1: The list of equipments/techniques used to test out the adsorbents characteristics.



3.1.1. Burned Palm Trunk

Raw palm trunk which was taken from plantation is cleaned by washing with water and last rinse with distilled water. After that, the sample was dried naturally for 24 hours and re-dried in oven, 160°C for a day to mock the burning process. It was then grinded to 2mm (2000µm) as shown in Figure 3.1



Figure 3.1: Grinded palm trunk

Figure 3.2 illustrates the results of Scanning Electron Microscopic (SEM) on the dried palm trunk porosity.

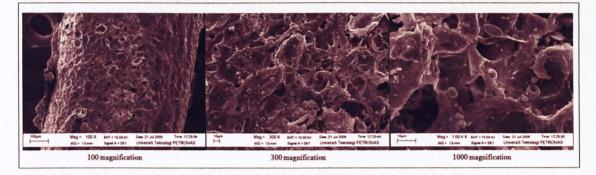


Figure 3.2: Scanning Electron Microscopic result of dried palm trunk (left to right: 100, 300 and 1000 magnification).

3.1.2. Cockle Shell Preparation

Raw cockle shell was washed with water with final rinse of distilled water. Then, come the most vital part. In preparing the cockle shell, the drying temperature was found to be the crucial factor to preserve the pore and protein. High temperature can cause protein de-nature and reduce the shell affinity towards heavy metal ions. Thus, the cockle shell was dried at different temperature and tested for its porosity and composition, as suggested below,

- 1. Natural drying
- 2. 40°C for 30 minutes
- 3. 100°C for 30 minutes

The dried shell then scanned by Scanning Electron Microscopic (SEM) to verify its porosity as shown in Figure 3.3. The naturally dried cockle shell was the most porous among all and no single porous void for the 100°C dried shell. Thus, the raw shell was utilized throughout the experiment. Moreover, this can increase the commercial value of the alternative adsorbent.

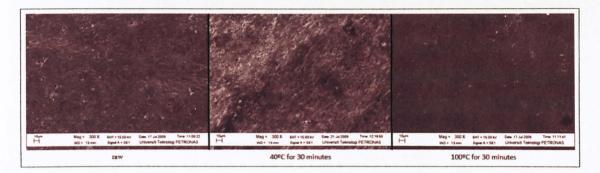


Figure 3.3: Scanning Electron Microscopic (SEM) result at 300 magnification (left to right: naturally dried, 40°C for 30 minutes and 100°C for 30 minutes)

Element	Naturally dried		Dried 100°C for 30 minutes	
Element	Weight %	Atomic %	Weight %	Atomic %
СК	16.80	26.61	11.07	17.38
ОК	47.44	56.42	57.59	67.88
Ca K	35.76	16.97	31.33	14.74

Table 3.2: Cockle	shell	element and	compound
-------------------	-------	-------------	----------

Standard:

C CaCO₃

O SiO₂

Ca Wollastonite

The selected dried cockle shell then grinded and sieved to 2mm (2000µm) as shown in Figure 3.4.



Figure 3.4: Cockle shell of Size 2mm (2000µm)

3.2. Preparation of Aqueous Solution

Stock solution of 1000 mg/L nickel was prepared before regulated to the preferred concentration. Stock solution was prepared by these following steps,

- 1. 4.9550g nickel nitrate was weighed in a Petri plate using a weighing machine.
- 2. The powder was diluted using distilled water.

 The solution was filled into 1L volumetric flask and distilled water was added to fulfill the flask.

The stock solution was then further diluted to the desired concentration by adding distillation water. The required amount of distilled water needed to make the dilution was equate by,

 $M_1V_1 = M_2V_2$

M: metal salt concentration, mg/L

V: solution volume, mL

For instance, in getting 200mg/L of metal in 250ml of water,

 $M_1V_1 = M_2V_2$

200mg/L x 250ml = 1000mg/L x V

 $V = \frac{200 \times 250}{1000}$ = 50 ml

3.3. Experiment Parameter

The experiments were carried out as a batch system using 18 beakers of volume 75 mL at a total sample volume of 30 mL for each adsorption run. All beakers will be placed on shaker at the same time. The system was done with initial solution concentration of 50 mg/L. The temperature and pressure were set at standard condition, 25°C and 14.7 psia respectively. In the other hand, for the adsorbent mass, it was weighed as calculated before placed in each of 18 beakers sample. The calculation was as follow,

For instance, for 1 g/L of adsorbent mass,

 $x = \frac{1g \times 30mL}{1000mL}$ x = 0.03g

Thus, each beaker of 30 mL solution will contain 0.03g of adsorbent.

Samples concentrations were measured at every 10 minutes time intervals. For sampling, the 0minute sample will be taken from first beaker, 10minute sample from second beaker and so on so forth. This to avoid the great volume reduction in the system that later will affect the result. The metal concentration in the sample was then measured by atomic absorption spectroscopy (AAS).

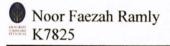
3.4. Adsorbent Mass Experiment

The experiment was repeated three times with different adsorbent mass, ranging from 1.0 - 10.0 g/L. Table 3.4 is adsorbent mass experiment matrix.

Adsorbents Mass (g/L)	Activated carbon	Burned palm trunk	Cockle shell
1.0			
5.0			
10.0			

Table 3.3: Adsorbent mass experiment matrix

The adsorbent mass experiment data will be plotted as removal percentage versus adsorbent dosage graph.

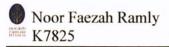


3.5. Experiment Data

For every experiment, initial concentration and metal concentration in solution were recorded. Table 3.5 generalized raw data obtain from the experiment

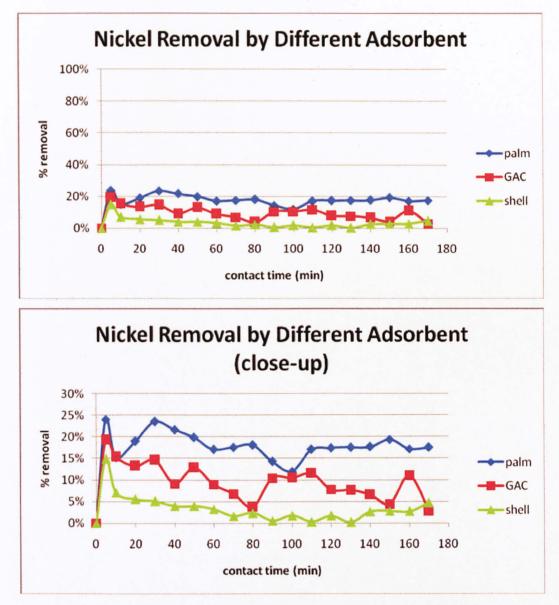
Time, minute	Metal concentration
0	
05	······································
10	
20	
30	
40	
50	
60	
70	
80	
90	
100	
110	
120	
130	
140	
150	
160	
170	

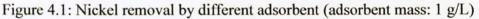
Table 3.4: Generalized raw data obtain from the experiment



4. RESULT AND DISCUSSION

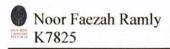
4.1. Effect of Different Adsorbent







The comparison between different adsorbents on the removal of nickel ion at $C_0 = 50$ mg/L was studied and result is represented in Figure 4.1. The nickel removal percentage was in the order of burned palm trunk > granular activated carbon (GAC) > cockle shell, 24%, 19% and 15% respectively. The highest metal loading was at fifth minute of contact time before it fluctuates within a range of 11%, 12%, and 7% for burned palm trunk, GAC and cockle shell respectively. Nickel removal is favored by palm trunk over industrial common practice which is GAC throughout the contact time and that makes it potential for cheaper adsorption alternative. Both palm trunk and GAC encompass carbonaceous material to bind heavy metals. Despite crustacean being stated as a promising adsorbent alternative, cockle shell shows the poorest performance among all adsorbents. Cockle shell however proved its capability in removing heavy metal. Sulfhydryl groups in the shell protein exhibit higher affinities towards heavy metal enable the adsorption process. Some modification should be made to enhance shell adsorption capability as it starts to desorb the removed metal. Desorption is a phenomenon whereby a substance is released from or through a surface. The process is the opposite of sorption. This occurs in a system being in the state of sorption equilibrium between bulk phase, in this case is the aqueous solution and an adsorbing surface. When the concentration or pressure of substance in the bulk phase is lowered, some of the sorbed substance changes to the bulk state.



4.2. Effect of Adsorbent Mass.

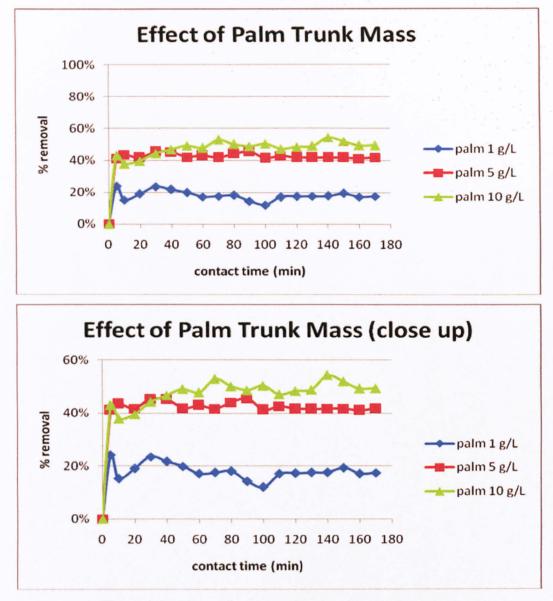


Figure 4.2: Effect of palm trunk mass on nickel removal

As expected, 1 g/L of palm trunk removed the lowest amount of nickel of all palm trunk mass, followed by 5 g/L and 10 g/L with removal percentage of 24%, 45% and 54% respectively. However, 5 g/L palm trunk was removing more nickel ion than 10 g/L palm trunk at early minutes. Biomass concentration in solution seems to influence the specific uptake. For lower values of biomass concentrations there is an increase in the



specific uptake. Gadd et al. 1988 suggested that an increase in biomass concentration leads to interference between the binding sites. Fourest and Roux, 1992 invalidated this hypothesis attributing the responsibility of the specific uptake decrease to metal concentration shortage in solution. However, this experiment showed there was interference between the binding sites at high adsorbent mass that decrease nickel loading onto the site. It can be concluded that, 50 mg/L of nickel is removed efficiently with palm trunk mass of 5 - 10 g/L.

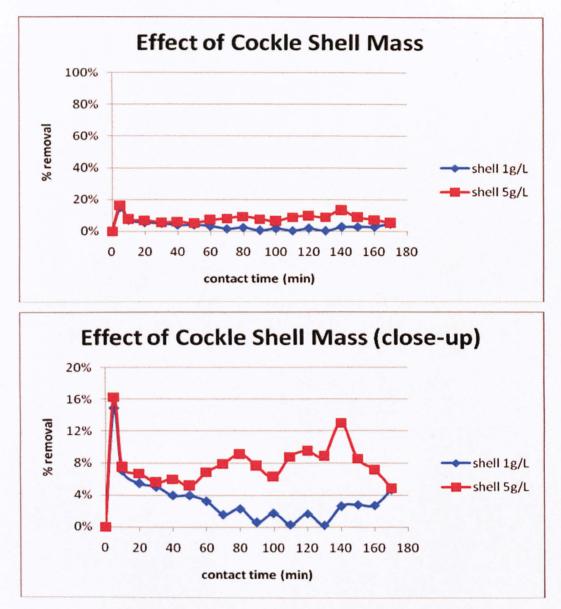


Figure 4.3: Effect of cockle shell mass on nickel removal

The removal percentage of nickel ion by cockle shell was found to increase with an increase in adsorbent dosage from 1 to 5 g/L. Increase in adsorption dosage attributed to the availability of larger surface area and more adsorption sites. At very low adsorbent concentration, the adsorbent surface becomes saturated with the metal ions and the residual metal ion concentration in the solution is large. With an increase in adsorbent dosage, the metal ion removal increases. It is also found that, the metal tends to desorp into the aqueous solution at low cockle shell concentration. Desorption is an opposite process of sorption, where a substance is released from or through a adsorption surface into solution. This occurs in a system being in the state of sorption equilibrium between bulk phase, in this case is the aqueous solution and an adsorbing surface. When the concentration or pressure of substance in the bulk phase is lowered, some of the sorbed substance changes to the bulk state. Some modification should be made to enhance shell adsorption capability as it starts to desorb the removed metal. Additive of copper can be added to the shell to trap metal and reinforce affinity.

4.3. Adsorption Isotherm

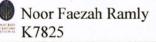
Adsorbent	Model (r ² value)		
Adsorbent	Langmuir	Freundlich	
Burned palm trunk	0.938	0.978	
Cockle shell	0.252	0.629	
Granular Activated Carbon	0.721	0.904	

Table 4.1: Comparison of r-squared value of different adsorbent

In these particular experimental ranges, Freundlich isotherm model was more appropriate than that of Langmuir model. The Freundlich adsorption isotherm is an adsorption isotherm, which is a curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. The Langmuir isotherm relates the coverage or adsorption of molecules on a



solid surface to gas pressure or concentration of a medium above the solid surface at a fixed temperature. The Langmuir adsorption isotherm describes quantitatively the build up of a layer of molecules on an adsorbent surface as a function of the concentration of the adsorbed material in the liquid in which it is in contact. In a modified form it can also describe a bi-layer deposition. Therefore, the uptake of nickel ion preferably not follows the heterolayer adsorption process.



5. CONCLUSION

In conclusion, this project has achieved its objectives in studying the capability of palm trunk and cockle shell in removing nickel ion and adsorbent mass effect on heavy metal ion removal. From experiment, palm trunk and cockle shell affinity towards nickel ion were proven, with decreasing order of burned palm trunk (24%) > granular activated carbon (19%) > cockle shell (15%). The removal percentage is proportional to adsorbent mass when more metal ion was removed if more adsorbent been put in. However, because of specific uptake, there was slight interference of adsorption process that influences the removal percentage. Nonetheless, the highest adsorbent mass shows the best performance. Other than that, cockle shell shows the tendencies to desorp the sorbed nickel ion into the solution. An optional analysis of adsorption isotherm equilibrium was done to study the relationship between sorbed nickel ion and remaining nickel ion in solution. From the r^2 value, this process followed Freundlich the best.

Listed are suggestion of recommendations and future works,

- 1. Detail study on temperature effect in adsorbent preparation step.
- 2. Study on possible cockle shell additive to improve its affinity.
- 3. Run experiment in real situation, i.e, system of battery industry waste

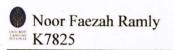
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7. APPENDICES

7.1. Nickel Metal Material Data Safety Sheet

Material Safety Data Sheet Nickel Metal

ACC# 16240

Section 1 - Chemical Product and Company Identification

MSDS Name: Nickel Metal Catalog Numbers: N40-500 Synonyms: Company Identification: Fisher Scientific 1 Reagent Lane Fair Lawn, NJ 07410 For information, call: 201-796-7100 Emergency Number: 201-796-7100 For CHEMTREC assistance, call: 800-424-9300 For International CHEMTREC assistance, call: 703-527-3887

Section 2 - Composition, Information on Ingredients

CAS#	Chemical Name	Percent	EINECS/ELINCS
7440-02-0	NICKEL	100.0	231-111-4

Section 3 - Hazards Identification

EMERGENCY OVERVIEW

Appearance: white to gray white solid.

Caution! May cause allergic skin reaction. May cause eye irritation. May cause respiratory tract irritation. May cause cancer in humans. May cause liver and kidney damage. **Target Organs:** Kidneys, liver, respiratory system.

Potential Health Effects

Eye: May cause eye irritation.

5kin: May cause skin sensitization, an allergic reaction, which becomes evident upon re-exposure to this material. May cause severe irritation and possible burns. May cause dermatitis.

Ingestion: Causes gastrointestinal irritation with nausea, vomiting and diarrhea.

Inhalation: Inhalation of fumes may cause metal fume fever, which is characterized by flu-like øymptoms with metallic taste, fever, chills, cough, weakness, chest pain, muscle pain and increased white blood cell count. Inhalation of a mist of this material may cause respiratory tract irritation. Breathing Nickel (Dust and Fume) can cause a sore or hole in the "bone" (septum) dividing the inner nose.

Chronic: Prolonged or repeated skin contact may cause sensitization dermatitis and possible destruction and/or ulceration. May cause respiratory tract cancer.

Section 4 - First Aid Measures

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Eyes: Flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical aid immediately.

Skin: Get medical aid if irritation develops or persists. Wash clothing before reuse. Flush skin with plenty of soap and water.

Ingestion: If victim is conscious and alert, give 2-4 cupfuls of milk or water. Never give anything by mouth to an unconscious person. Get medical aid immediately.

Inhalation: Remove from exposure and move to fresh air immediately. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical aid if cough or other symptoms appear.

Notes to Physician: Treat symptomatically and supportively.

Antidote: There exists several chelation agents. The determination of there use should be made only by qualified medical personnel.

Section 5 - Fire Fighting Measures

General Information: As in any fire, wear a self-contained breathing apparatus in pressuredemand, MSHA/NIOSH (approved or equivalent), and full protective gear. Dusts at sufficient concentrations can form explosive mixtures with air. During a fire, irritating and highly toxic gases may be generated by thermal decomposition or combustion. Dust can be an explosion hazard when exposed to heat or flame.

£xtinguishing Media: Confining and smothering is preferable to applying water. DO NOT USE WATER, CO2, OR FOAM DIRECTLY ON FIRE ITSELF. Use DRY sand, sodium chloride powder, graphite powder, copper powder or Lith-X powder. Dousing metallic fires with water may generate nydrogen gas, an extremely dangerous explosion hazard, particularly if fire is in a confined environment.

Flash Point: Not applicable.

Autoignition Temperature: Not applicable.

Explosion Limits, Lower:Not available.

Upper: Not available.

NFPA Rating: (estimated) Health: 3; Flammability: 1; Instability: 0

Section 6 - Accidental Release Measures

General Information: Use proper personal protective equipment as indicated in Section 8. **Ppills/Leaks:** Very fine particles can cause a fire or explosion. Eliminate all ignition sources. Reduce airborne dust and prevent scattering by moistening with water. Sweep up, then place into a puitable container for disposal. Carefully scoop up and place into appropriate disposal container. Provide ventilation.

Section 7 - Handling and Storage

andling: Wash thoroughly after handling. Remove contaminated clothing and wash before reuse. Ise with adequate ventilation. Minimize dust generation and accumulation. Avoid contact with skin and eyes. Avoid ingestion and inhalation.

Storage: Store in a cool, dry, well-ventilated area away from incompatible substances. Keep ontainers tightly closed.

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Section 8 - Exposure Controls, Personal Protection

Engineering Controls: Facilities storing or utilizing this material should be equipped with an eyewash facility and a safety shower. Use adequate general or local exhaust ventilation to keep airborne concentrations below the permissible exposure limits.

Exposure Limits

Chemical Name	ACGIH	NIOSH	OSHA - Final PELs
NICKEL	1.5 mg/m3 TWA (inhalable fraction)	0.015 mg/m3 TWA 10 mg/m3 IDLH	1 mg/m3 TWA

OSHA Vacated PELs: NICKEL: 1 mg/m3 TWA Personal Protective Equipment

Eyes: Wear appropriate protective eyeglasses or chemical safety goggles as described by OSHA's eye and face protection regulations in 29 CFR 1910.133 or European Standard EN166. **Skin:** Wear appropriate gloves to prevent skin exposure.

Clothing: Wear appropriate protective clothing to minimize contact with skin.

Respirators: Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced.

Section 9 - Physical and Chemical Properties

Physical State: Solid
Appearance: white to gray white
Odor: none reported
pH: Not available.
Vapor Pressure: 1 mm Hg @ 1810 C
Vapor Density: Not available.
Fvaporation Rate:Not available.
Viscosity: Not applicable.
Boiling Point: 2730 deg C
Freezing/Melting Point:1455 deg C
Pecomposition Temperature:Not available.
Solubility: Insoluble in water.
Specific Gravity/Density:8.90
Molecular Formula:Ni

Section 10 - Stability and Reactivity

Chemical Stability: Stable under normal temperatures and pressures.

Conditions to Avoid: Incompatible materials, dust generation.

Incompatibilities with Other Materials: Acids, aluminum, ammonia, ammonium nitrate,

promine pentafluoride, ethylene + aluminum, dioxane, fluorine, hydrazine, hydrazoic acid,

ydrogen, methanol, nitric acid, nitryl fluoride, organic solvents, oxidants, phosphorus, potassium perchlorate, selenium, sulfur and compounds.

lazardous Decomposition Products: Toxic and highly flammable nickel carbonyl.

azardous Polymerization: Has not been reported.

Section 11 - Toxicological Information

RTECS#:

CAS# 7440-02-0: QR5950000; QR6126100; QR6555000; QR7120000 LD50/LC50: Not available.

Carcinogenicity:

CAS# 7440-02-0:

- ACGIH: Not listed.
- California: carcinogen, initial date 10/1/89
- NTP: Suspect carcinogen
- IARC: Group 1 carcinogen (listed as Nickel compounds).

pidemiology: Epidemiological studies have shown an increased incidence of cancers among nickel refinery workers.
 reratogenicity: No information available.
 Reproductive Effects: No information available.

Autagenicity: No information available.

Other Studies:

Section 12 - Ecological Information

Cotoxicity: No data available. No information available. **Invironmental:** No information reported. **Physical:** No information available. **Other:** None.

Section 13 - Disposal Considerations

Chemical waste generators must determine whether a discarded chemical is classified as a nazardous waste. US EPA guidelines for the classification determination are listed in 40 CFR Parts 761.3. Additionally, waste generators must consult state and local hazardous waste regulations to insure complete and accurate classification.

ACRA P-Series: None listed.

ACRA U-Series: None listed.

Section 14 - Transport Information

	US DOT	Canada TDG
Shipping Name:	Not regulated as a hazardous material	No information available.
Hazard Class:		
UN Number:		

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Packing Group:

Section 15 - Regulatory Information

US FEDERAL

TSCA

CAS# 7440-02-0 is listed on the TSCA inventory.

Health & Safety Reporting List

None of the chemicals are on the Health & Safety Reporting List.

Chemical Test Rules

None of the chemicals in this product are under a Chemical Test Rule.

Section 12b

None of the chemicals are listed under TSCA Section 12b.

TSCA Significant New Use Rule

None of the chemicals in this material have a SNUR under TSCA.

CERCLA Hazardous Substances and corresponding RQs

CAS# 7440-02-0: 100 lb final RQ (no reporting of releases of this hazardous substance is require

SARA Section 302 Extremely Hazardous Substances

None of the chemicals in this product have a TPQ.

SARA Codes

CAS # 7440-02-0: immediate, delayed, fire.

Section 313

This material contains NICKEL (CAS# 7440-02-0, 100.0%), which is subject to the reporting requirements of Section 313 of SARA Title III and 40 CFR Part 373.

Clean Air Act:

CAS# 7440-02-0 (listed as Nickel compounds) is listed as a hazardous a ir pollutant (HAP). This material does not contain any Class 1 Ozone depletors.

This material does not contain any Class 2 Ozone depletors.

Clean Water Act:

None of the chemicals in this product are listed as Hazardous Substances under the CWA. Water Act. CAS# 7440-02-CAS# 7440-02-0 is listed as a Priority Pollutant under the Clean

0 is listed as a Toxic Pollutant under the Clean Water Act.

OSHA:

None of the chemicals in this product are considered highly hazardous by OSHA. STATE

CAS# 7440-02-0 can be found on the following state right to know lists: California, New Jersey, Pennsylvania, Minnesota, Massachusetts.

California Prop 65

The following statement(s) is(are) made in order to comply with the California Safe **Drinking Water Act:**

WARNING: This product contains NICKEL, a chemical known to the state of California to cause cancer.

California No Significant Risk Level: None of the chemicals in this product are listed.

European/International Regulations

European Labeling in Accordance with EC Directives Hazard Symbols:

XN

Risk Phrases:

R 40 Limited evidence of a carcinogenic effect.

R 43 May cause sensitization by skin contact.

Safety Phrases:

S 22 Do not breathe dust.

S 36 Wear suitable protective clothing.

WGK (Water Danger/Protection)

CAS# 7440-02-0: No information available.

Canada - DSL/NDSL

CAS# 7440-02-0 is listed on Canada's DSL List.

Canada - WHMIS

This product has a WHMIS classification of D2A.

This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations and the MSDS contains all of the information required by those regulations.

Canadian Ingredient Disclosure List

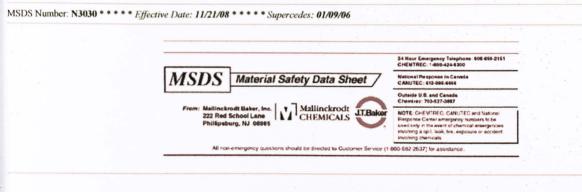
CAS# 7440-02-0 is listed on the Canadian Ingredient Disclosure List.

Section 16 - Additional Information

MSDS Creation Date: 3/19/1998 Revision #5 Date: 10/28/2008

The information above is believed to be accurate and represents the best information currently available to us. However, we make no warranty of merchantability or any other warranty, express or implied, with respect to such information, and we assume no liability resulting from its use. Users should make their own investigations to determine the suitability of the information for their particular purposes. In no event shall Fisher be liable for any claims, losses, or damages of any third party or for lost profits or any special, indirect, incidental, consequential or exemplary damages, howsoever arising, even if Fisher has been advised of the possibility of such damages.

7.2. Nickel Nitrate Material Data Safety Sheet



NICKEL NITRATE

1. Product Identification

Synonyms: Nickel (II) nitrate, hexahydrate (1:2:6); nickelous nitrate; nitric acid, nickel (2+) salt, hexahydrate; Nickelous nitrate, 6- Hydrate CAS No.: 13138-45-9 Anhydrous; (13478-00-7 Hexahydrate) Molecular Weight: 290.83 Chemical Formula: Ni(NO3)2 6H2O **Product Codes:** J.T. Baker: 2784 Mallinckrodt: 6384

2. Composition/Information on Ingredients

Ingredient	CAS No	Percent	Hazardous
Nickel Nitrate	13138-45-9	90 - 100%	Yes

3. Hazards Identification

Emergency Overview

DANGER! STRONG OXIDIZER. CONTACT WITH OTHER MATERIAL MAY CAUSE FIRE. HARMFUL IF SWALLOWED OR INHALED. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT. MAY CAUSE ALLERGIC SKIN OR RESPIRATORY REACTION. CANCER HAZARD. CAN CAUSE CANCER. Risk of cancer depends on duration and level of exposure. Very toxic to aquatic organisms; may cause long term adverse effects in the aquatic environment.

SAF-T-DATA(tm) Ratings (Provided here for your convenience)

Health Rating: 3 - Severe (Cancer Causing) Flammability Rating: 0 - None Reactivity Rating: 3 - Severe (Oxidizer) Contact Rating: 3 - Severe (Life) Lab Protective Equip: GOGGLES & SHIELD; LAB COAT & APRON; VENT HOOD; PROPER GLOVES Storage Color Code: Yellow (Reactive)

Potential Health Effects

Inhalation:

Causes irritation to the respiratory tract. Symptoms may include coughing, sore throat, and shortness of breath. Lung damage may result from a single high exposure or lower repeated exposures. Lung allergy occasionally occurs, with asthma type symptoms.

Ingestion:

Toxic. Symptoms may include abdominal pain, diarrhea, nausea, and vomiting. Absorption is poor, but should it occur, symptoms may include giddiness, capillary damage, myocardial weakness, central nervous system depression, and kidney and liver damage.

Skin Contact: Causes irritation. May cause skin allergy with itching, redness or rash. Some individuals may become sensitized to the substance and suffer "nickel itch", a form

of dermatitis.

Eve Contact:

Causes irritation, redness, and pain.

Chronic Exposure:

Prolonged or repeated exposure to excessive concentrations may affect lungs, liver and kidneys. Chronic exposure to nickel and nickel compounds is associated with cancer

Aggravation of Pre-existing Conditions:

Persons with pre-existing skin disorders, impaired respiratory or pulmonary function, or with a history of asthma, allergies, or sensitization to nickel compounds

may be at an increased risk upon exposure to this substance

4. First Aid Measures

Inhalation:

Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention. Ingestion:

Induce vomiting immediately as directed by medical personnel. Never give anything by mouth to an unconscious person. Get medical attention

Skin Contact:

Wipe off excess material from skin then immediately flush skin with plenty of water for at least 15 minutes. Remove contaminated clothing and shoes. Get medical attention. Wash clothing before reuse. Thoroughly clean shoes before reuse. Eye Contact:

Immediately flush eyes with plenty of water for at least 15 minutes, lifting lower and upper eyelids occasionally. Get medical attention immediately.

5. Fire Fighting Measures

Fire:

Not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition. Increases the flammability of any combustible material. **Explosion:**

Contact with oxidizable substances may cause extremely violent combustion. Strong oxidants may explode when shocked, or if exposed to heat, flame, or friction. Also may act as initiation source for dust or vapor explosions.

Fire Extinguishing Media:

Water or water spray in early stages of fire. Foam or dry chemical may also be used.

Special Information:

Wear full protective clothing and breathing equipment for high-intensity fire or potential explosion conditions.

6. Accidental Release Measures

Remove all sources of ignition. Ventilate area of leak or spill. Wear appropriate personal protective equipment as specified in Section 8. Spills: Clean up spills in a manner that does not disperse dust into the air. Use non-sparking tools and equipment. Reduce airborne dust and prevent scattering by moistening with water. Pick up spill for recovery or disposal and place in a closed container.

7. Handling and Storage

Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage and moisture. Isolate from any source of heat or ignition. Avoid storage on wood floors. Separate from incompatibles, combustibles, organic or other readily oxidizable materials. Areas in which exposure to nickel metal or soluble nickel compounds may occur should be identified by signs or appropriate means, and access to the area should be limited to authorized persons. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

8. Exposure Controls/Personal Protection

Airborne Exposure Limits:

-OSHA Permissible Exposure Limit (PEL): soluble Nickel compounds as Ni: 1 mg/m3 (TWA) -ACGIH Threshold Limit Value (TLV): soluble Nickel compounds as Ni: 0.1 mg/m3 (TWA), A4 - Not classifiable as a human carcinogen Ventilation System: A system of local and/or general exhaust is recommended to keep employee exposures below the Airborne Exposure Limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, Industrial Ventilation, A Manual of Recommended Practices, most recent edition, for details. Personal Respirators (NIOSH Approved): If the exposure limit is exceeded and engineering controls are not feasible, a full facepiece particulate respirator (NIOSH type N100 filters) may be worn for up to 50 times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. If oil particles (e.g. lubricants, cutting fluids. glycerine, etc.) are present, use a NIOSH type R or P filter. For emergencies or instances where the exposure levels are not known, use a full-facepiece positive-pressure, air-supplied respirator. WARNING: Air-purifying respirators do not protect workers in oxygen-deficient atmospheres Skin Protection: Rubber or neoprene gloves and additional protection including impervious boots, apron, or coveralls, as needed in areas of unusual exposure.

Eye Protection: Use chemical safety goggles and/or full face shield where dusting or splashing of solutions is possible. Maintain eye wash fountain and quick-drench facilities in

work area.

Other Control Measures:

Eating, drinking, and smoking should not be permitted in areas where solids or liquids containing soluble nickel compounds are handled, processed, or stored. NIOSH recommends pre-placement and periodic medical exams, with maintaining of records for all employees exposed to nickel in the workplace.

9. Physical and Chemical Properties

Appearance: Green, transparent crystals. Odor: Odorless Solubility: 238.5g/100cc water @ 0C Specific Gravity: 2.05 pH: 3.5 - 5.5 (5% solution @ 25C (77F) % Volatiles by volume @ 21C (70F): 0 **Boiling Point:** 137C (279F) **Melting Point:** 56.7C (135F) Vapor Density (Air=1): No information found. Vapor Pressure (mm Hg): 0 @ 20C (68F) Evaporation Rate (BuAc=1): No information found.

10. Stability and Reactivity

Stability:

Stable under ordinary conditions of use and storage. Substance has both oxidant and reducing characteristics, and is unstable when heated or shocked. Hazardous Decomposition Products: Emits toxic fumes of nickel and nitrogen oxides when heated to decomposition. Hazardous Polymerization: Will not occur. Incompatibilities: Aluminum, boron phosphide, cyanides, esters, combustible material, phospham, phosphorus, sodium hypophosphite, stannous chloride, thiocyanates, strong reducing agents, and organic materials. Conditions to Avoid: Heat, shock, friction, incompatibles.

11. Toxicological Information

Nickelous Nitrate Hexahydrate; Oral rat LD50: 1620 mg/kg. Investigated as a tumorigen.

	NTP	Carcinogen	
Ingredient	Known	Anticipated	IARC Category
Nickel Nitrate (13138-45-9)	Yes	No	1

12. Ecological Information

Environmental Fate: When released into water, this material is not expected to evaporate significantly. This material is not expected to significantly bioaccumulate. Environmental Toxicity: Dangerous to the environment. Very toxic to aquatic organisms; may cause long term adverse effects in the aquatic environment.

13. Disposal Considerations

Whatever cannot be saved for recovery or recycling should be handled as hazardous waste and sent to a RCRA approved waste facility. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations. Dispose of container and unused contents in accordance with federal, state and local requirements.

14. Transport Information

Domestic (Land, D.O.T.)

Proper Shipping Name: NICKEL NITRATE Hazard Class: 5.1 UN/NA: UN2725 Packing Group: III Information reported for product/size: 4X25LB

International (Water, LM.O.)

15. Regulatory Information

Ingredient		TSCA			Australia
Nickel Nitrate (13138-45-9)		Yes	Yes	Yes	Yes
\Chemical Inventory Status - Part	t 2\	00 00 00 00 00 No on Ot			
			Ca	inada	
Ingredient		Korea	DSL	NDSL	Phil.
Nickel Nitrate (13138-45-9)		Yes	Yes	No	Yes
(Federal, State & International 1					
	-SAR RQ	A 302- TPQ	Lis	st Che	A 313 mical Catg
Ingredient	-SAR	A 302-	Lis	st Che	A 313 mical Catg
Ingredient Nickel Nitrate (13138-45-9)	-SAR RQ No	A 302- TPQ No ions -	Li: No Part 2	st Che Nic	A 313 mical Catg kel cmpd/
Ingredient Nickel Nitrate (13130-45-9) \Federal, State & International I	-SAR RQ No Regulat	A 302- TPQ No ions -	Li: No Part 2 -RCRA-	St Che Nic	A 313 mical Catg kel cmpd/ SCA-
	-SAR RQ No	A 302- TPQ No ions - LA	Li: No Part 2 -RCRA-	SAR st Che Nic 2\ 3 8	A 313 mical Catg kel cmpd/ SCA-

Chemical Weapons Convention: No TSCA 12(b): No CDTA: NO GARA 311/312: Acute: Yes Chronic: Yes Fire: No Pressure: No geactivity: Yes (Pure / Solid)

WARNING:

THIS PRODUCT CONTAINS A CHEMICAL(S) KNOWN TO THE STATE OF CALIFORNIA TO CAUSE CANCER.

Australian Hazchem Code: 1Y Poison Schedule: None allocated.

WHMIS:

This MSDS has been prepared according to the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all of the information required by the CPR.

16. Other Information

NFPA Ratings: Health: 1 Flammability: 0 Reactivity: 0 Other: Oxidizer

Label Hazard Warning:

DANGER! STRONG OXIDIZER. CONTACT WITH OTHER MATERIAL MAY CAUSE FIRE. HARMFUL IF SWALLOWED OR INHALED. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT. MAY CAUSE ALLERGIC SKIN OR RESPIRATORY REACTION. CANCER HAZARD. CAN CAUSE CANCER. Risk of cancer depends on duration and level of exposure. Very toxic to aquatic organisms; may cause long term adverse effects in the aquatic environment.

Label Precautions: Do not store near combustible materials. Do not get in eyes, on skin, or on clothing

Remove and wash contaminated clothing promptly.

Wash thoroughly after handling.

Do not breathe dust.

Keep container closed. Use only with adequate ventilation.

Avoid release to the environment.

Label First Aid:

If swallowed, induce vomiting immediately as directed by medical personnel. Never give anything by mouth to an unconscious person. If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. In case of contact, wipe off excess material from skin then immediately flush eyes or skin with plenty of water for at least 15 minutes. Remove contaminated clothing and shoes. Wash clothing before reuse. In all cases, get medical attention.

Product Use: Laboratory Reagent **Revision Information:** No Changes Disclaimer

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Prepared by: Environmental Health & Safety

Phone Number: (314) 654-1600 (U.S.A.)

7.3. Nickel Cadmium Battery Material Data Safety Sheet

NICKEL-CADMIUM BATTERIES



MATERIAL SAFETY DATA SHEET

BATTERY MANUFACTURER'S MSDS DISTRIBUTED BY: HUBBELL LIGHTING, INC.

PRODUCT NAME: NICKEL-CADMIUM BATTERIES

DATE: January 1, 2007

HAZARDOUS INGREDIENTS

IMPORTANT NOTE: THE BATTERY SHOULD NOT BE OPENED OR BURNED. EXPOSURE TO THE INGREDIENTS CONTAINED WITHIN OR THEIR COMBUSTION PRODUCTS COULD BE HARMFUL.

MATERIAL OR INGREDIENTS	% W. t.
Cadmium as Cadmium Metal (CAS # 7440-43-9) Cadmium Oxide (CAS # 1306-19-0) Cadmium Hydroxide (CAS # 21041-95-2)	8-22
Cobalt as Cobalt Metal (CAS # 7440-48-4) Cobalt Oxide (CAS # 1307-96-6) Cobalt Hydroxide (CAS # 21041-93-0)	1-2
Lithium Hydroxide (CAS # 1310-65-2)	0-1
Nickel as Nickel Metal (CAS # 7440-02-0) Nickel Oxide (CAS # 1313-99-1) Nickel Hydroxide (CAS # 12054-48-7)	20-30
Potassium Hydroxide (CAS # 1310-58-3)	0-5

FIRE AND EXPLOSION HAZARD DATA

If fire or explosion occurs when batteries are on charge, shut off power to charge.

In case of fire, it is permissable to use any class of extinguishing medium on these batteries or their packing materials. Cool exterior of batteries if exposed to fire to prevent rupture.

Fire fighters should wear self-contained breathing apparatus. Nickel-Cadmium batteries involved in a fire can vent and produce toxic fumes including nickel, nickel oxide, cadmium, cadmium oxides, and cobalt oxides.

HEALTH HAZARD DATA

Under normal conditions of use, the battery is hermetically sealed.

INGESTION: Swallowing a battery can be harmful. Contents of an open battery can cause serious chemical burns of mouth, esophagus, and gastrointestinal tract. Contents include toxic cadmium compounds that can cause excessive salivation, choking, nausea, persistent vomiting, diarrhea, abdominal pain, dizziness, faintness, unconsciousness, and possible liver and kidney injury.

If a battery or open battery is ingested, do not induce vomiting or give food or drink. Seek medical attention immediately.

INHALATION: Contents of an open battery can cause respiratory irritation. Cadmium oxide fumes can cause metal fume fever. Hypersensitivity to nickel can cause allergic pulmonary asthma. Provide fresh air and seek medical attention.

SKIN CONTACT: Contents of an open battery can cause skin irritation and/or chemical burns. Cobalt, cobalt compounds, nickel and nickel compounds can cause skin sensitization and an allergic contact dermatitis. Remove contaminated clothing and wash skin with soap and water. If a chemical burn occurs or if irritation persists, seek medical attention.

EYE CONTACT: Contents of an open battery can cause severe irritation and chemical burns. Immediately flush eyes thoroughly with water for at least 15 minutes, lifting upper and lower lids, until no evidence of the chemical remains. Seek medical attention.

PRECAUTIONS FOR SAFE HANDLING AND USE

STORAGE: Store in a cool, well-ventilated area. Elevated temperature can result in shortened battery life.

MECHANICAL CONTAINMENT: Do not obstruct safety release vents on batteries. Encapsulation of batteries will not allow cell venting and can cause high-pressure rupture.

HANDLING: Accidental short circuit for a few seconds will not seriously affect the battery. However, this battery is capable of delivering very high short circuits. Prolonged short circuits will cause high cell temperatures that can cause skin burns. Sources of short circuits include jumbled batteries in bulk containers, metal jewelry, and metal covered tables or metal belts used for assembly of batteries into devices.

If soldering or welding to the battery is required, use of tabbed batteries is recommended.

Do not open battery. The negative electrode material may be pyrophoric. Should an individual cell from a battery become disassembled, spontaneous combustion of the negative electrode is possible. That is much more likely to happen if the electrode is removed from its metal container. There can be a delay between exposure to air and spontaneous combustion.

CHARGING: This battery is made to be charged many times. Because it gradually loses its charge over a few months, it is good practice to charge battery before use. Use recommended charger. Improper charging can cause heat damage or even high pressure rupture. Observe proper charging polarity.

SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS: Not necessary under normal conditions.

RESPIRATORY PROTECTION: Not necessary under normal conditions.

EYE PROTECTION: Not necessary under normal conditions. Wear safety glasses with side shields if handling an open or leaking battery.

GLOVES: Not necessary under normal conditions. Use neoprene or natural rubber gloves if handling an open or leaking battery.

OPEN BATTERY STORAGE: Battery should not be opened. Should a cell become disassembled, the electrode should be stored in a fireproof cabinet, away from combustibles.

TRANSPORT INFORMATION

The product described is not covered by the international guidelines for the transport of dangerous substances.

UN Hazard CLASS: N/A UN Number : N/A

This is to certify that the above mentioned products are categorized as "nonspillable wet electric storage battery" according to Code of Federal Regulation (CFR) Title 49 (revised as of Oct. 1, 2001 issued by Department of Transportation) and exempted from all requirements for Hazardous Materials under the following conditions [CFR 49, Part 173, Section 159, Paragraphs (d)]:

1) The battery is protected against short circuit and securely packaged.

2) The battery is capable of withstanding the following two tests without leakage of battery fluid from the battery:

a. Vibration test

b. Pressure differential test

ADDITIONAL INFORMATION

This Material Safety Data Sheet is supplied for informational purposes only. The information and recommendations contained herein have been compiled from sources believed to be reliable and represent current opinion on the subject. No warranty, guarantee, or representation is made by the manufacturer and/or the supplier as to the absolute correctness or sufficiency of any representation contained herein and the manufacturer and/or the supplier assumes no responsibility in connection therewith, nor can it be assumed that all acceptable safety measures are contained herein, or that additional measures may not be required under particular or exceptional conditions or circumstances.

7.4. Nickel Metal Anhydride Battery Material Data Safety Sheet



MATERIAL SAFETY DATA SHEET

1. We would like to inform our customers that these batteries are exempt articles and are not subject to the 29 CFR 1910.1200 OSHA requirement, or to the Canadian WHMIS requirements and the sheets are supplied as a service to you. For other MSDSs and related information, visit: <u>http://www.rayovac.com/technical/msds.htm.</u>

1. IDENTIFICATION

PRODUCT NAME: Nickel Metal Hydride Batteries

SIZES: All

EMERGENCY TELEPHONE NUMBER: 800-424-9300 (24 hr, Chemtrec)

Environmental Health & Safety Information: 608-275-2482

EDITION DATE: 03/05/2007

APPROVED BY: Kevin J. Domack

2. INGREDIENTS

INGREDIENT NAME	CAS #	%	TLV*
Nickel and compounds	7440-02-0	30-40	1.0 mg/m ³ (Soluble Compounds, TWA)
Steel		15 - 25	
Potassium Hydroxide	1310-58-3	10-15	Not Listed
Cobalt and compounds	7440-48-4	4-8	$0.1 \text{ mg/m}^3 (\text{TWA})$
Manganese	7439-96-5	<2	C5.0 mg/m ³ (TWA)
Aluminum	7429-90-5	<1	15 mg/m ³ (Total Dust, TWA)
Lanthanides, Zinc	7440-66-6(Zn)	5 - 20	5 mg/m ³ (ZnO, Fume, TWA)
Water, paper, plastic, other		Balance	

*Source: OSHA 29 CFR 1910.1000 Table Z-1, 2 or 3 3-01-2007

3. PHYSICAL DATA

Boiling Point @ 760 mm Hg (°C):	NA
Vapor Pressure (mm Hg @ 25°C):	NA
Vapor Density (Air $= 1$):	NA
Density (grams/cc):	NA
Percent Volatile by Volume (%):	NA
Evaporation Rate (Butyl Acetate = 1):	NA
Physical State:	NA
Solubility in Water (% by Weight):	NA
pH:	NA
Appearance and Odor:	geometric solid object

4. FIRE & EXPLOSION HAZARD DATA

FLASH POINT:	NA	LOWER (LEL):	NA
FLAMMABLE LIMITS IN AIR (%):	NA	UPPER (UEL):	NA
EXTINGUISHING MEDIA:	Use water, foam or dr	y powder, as appropriate.	
AUTO-IGNITION:	NA		

<u>SPECIAL FIRE FIGHTING PROCEDURES</u>: As with any fire, wear self-contained breathing apparatus to avoid inhalation of hazardous decomposition products (See section 2).

<u>SPECIAL FIRE EXPLOSION HAZARDS</u>: Like any sealed container, battery cells may rupture when exposed to excessive heat; this could result in the release of flammable or corrosive materials.

5. HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE (TLV) AND SOURCE: NA

EFFECTS OF OVEREXPOSURE: None. (In fire or rupture situation see section 2 and section 4)

EMERGENCY FIRST AID PROCEDURES:

Skin and Eyes:

In the event that battery ruptures, flush exposed skin with copious quantities of flowing lukewarm water for a minimum of 15 minutes. Get immediate medical attention for eyes. Wash skin with soap and water. *Swallowing:*

Ingestion of a battery can be harmful. Call The National Capital Poison Center (800-222-1222), day or night, for advice and follow-up.

For more information, visit: http://www.nema.org/gov/ehs/committees/drybat/

6. REACTIVITY DATA

STABLE OR UNSTABLE:	Stable
INCOMPATIBILITY (MATERIALS TO AVOID):	NA
HAZARDOUS DECOMPOSITION PRODUCTS:	NA
DECOMPOSITION TEMPERATURE (0°F):	NA
HAZARDOUS POLYMERIZATION:	Will Not Occur
CONDITIONS TO AVOID:	Avoid electrical shorting.

7. SPILL OR LEAK PROCEDURES

PROCEDURES TO CONTAIN AND CLEAN UP LEAKS OR SPILLS: In the event of a battery rupture, prevent skin contact and collect all released material in a plastic lined metal container.

REPORTING PROCEDURE: Report all spills in accordance with Federal, State and Local reporting requirements.

WASTE DISPOSAL METHOD: Waste Nickel Metal Hydride Batteries are NOT considered a USEPA Hazardous Waste. Their collection and recycling are not required under US Federal Law. Contact your battery distributor for details regarding recycling and disposal options or visit; http://www.rbrc.org. For additional information on disposal or recycling options, visit: http://www.nema.org/gov/ehs/committees/drvbat/

PROTECTION INFORMATION 8.

RESPIRATORY PRO	DTECTION (SPECIFY TYPE):	NA	
VENTILATION:	Local Exhaust:	NA	
	Mechanical (General):	NA	
	Special:	NA	
	Other:	NA	
PROTECTIVE GLO	VES:	NA	
EYE PROTECTION		NA	
OTHER PROTECTI	VE CLOTHING:	NA	

9. SPECIAL PRECAUTIONS

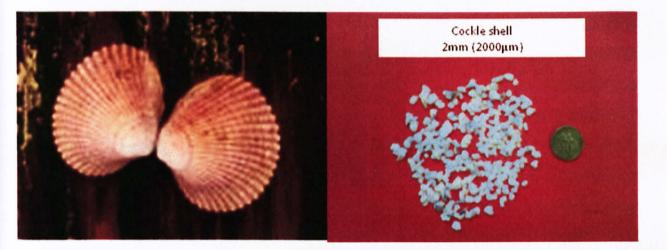
HANDLING AND STORAGE: Store in a dry place. Storing unpackaged cells together could result in cell shorting and heat build-up.

TRANSPORTATION-SHIPPING: These are "batteries, dry" and are not considered to be a "hazardous material" per the Dept. of Transportation (USDOT) regulations or "dangerous goods" per the International Air Transport Association (IATA) regulations. Shipments must comply with the general duty clause of USDOT 49 CFR 172.102 (a) (1) special provision 130, "to prevent shorting potential while transporting."

10. **SARA 313**

Notification is not required because these products are article(s) that do not release a covered toxic chemical under the normal conditions of processing or use.

NOTICE: The information and recommendations set forth are made in good faith and are believed to be accurate at the date of preparation. Rayovac Corporation makes no warranty expressed or implied.

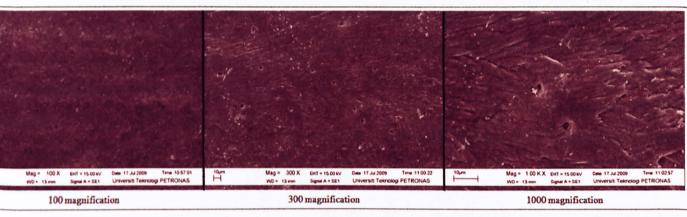




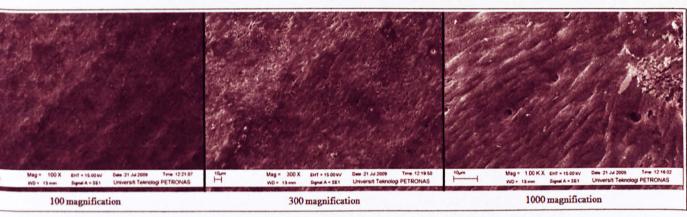
Burned palm trunk 2mm (2000 µm)



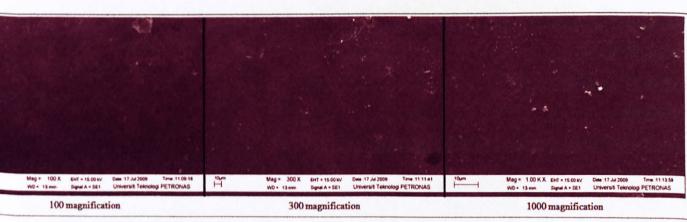
Dried at ambient condition



Dried at 40°C



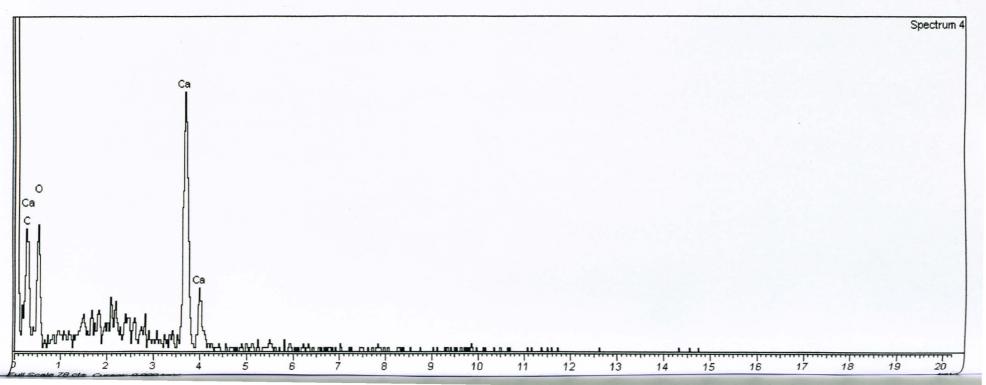
Dried at 100°C



Project 1

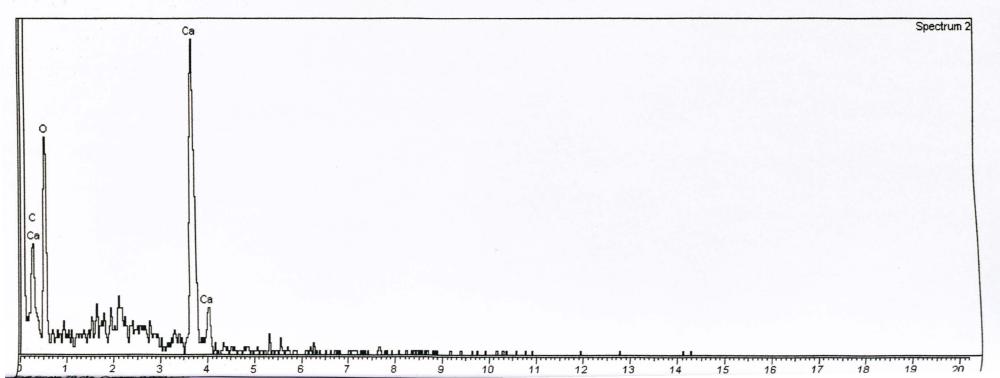
EDX Result: Dried at ambient condition

Comment:	Spectrum p No peaks o	-					
		Processing option : All elements analyzed (Normalised) Number of iterations = 4					
	O SiO2 1 Ca Wollas		:00 AM -1999 12:00 AM				
	Element	Weight%	Atomic%				
	СК	16.80	26.61				
	ОК	47.44	56.42				
	Ca K	35.76	16.97				
	Totals	100.00					



Project 1

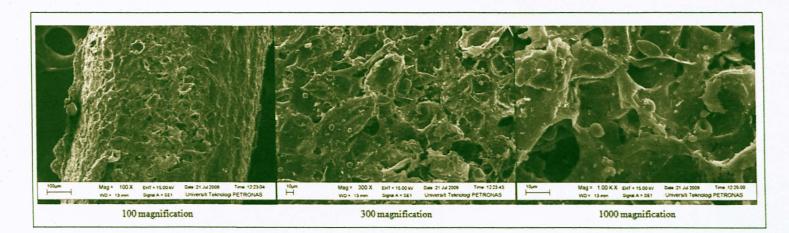
Comment:	Spectrum p No peaks of	-			
	Processing option : All elements analyzed (Normalised) Number of iterations = 5 Standard : C CaCO3 1-Jun-1999 12:00 AM O SiO2 1-Jun-1999 12:00 AM Ca Wollastonite 1-Jun-1999 12:00 AM				
	Element	Weight%	Atomic%		
	СК	11.07	17.38		
	СК	11.07 57.59	17.38 67.88		



EDX Result: Dried at 100 °C

7.9. SEM Result of Burned Palm Trunk

Dried at 160°C



7.10. AAS Result

17 0

47.67

Adsorbent size	: 2 mm
pН	:7
Nickel initial concentration	: 50 mg/L
Temperature	: 25°C
Pressure	: Atmosphere p

5%

41.24

8.76

18%

48.63

2.33

oncent	ELL 1g/L																
			PA	LM 1g/L		G	AC 1g/L		SH	ELL 5g/L		PA	LM 5g/L		PA	LM 10g/L	
ppm	Adsor bed. ppm	% rem oval	Concent ration, ppm	Adsor bed. ppm	% rem oval	Concent ration, ppm	Adsor bed. ppm	% rem oval	Concent ration, ppm	Adsor bed. ppm	% rem oval	Concent ration, ppm	Adsor bed. ppm	% rem oval	Concent ration, ppm	Adsor bed. ppm	% rem oval
50.00	0.00	0%	50.00	0.00	0%	50.00	0.00	0%	50.00	0.00	0%	50.00	0.00	0%	50.00	0.00	0%
42.55	7.45	15%	37.99	12.01	24%	40.36	9.64	19%	41.85	8.15	16%	29.43	20.57	41%	28.50	21.50	43%
46.49	3.51	7%	42.41	7.59	15%	42.34	7.66	15%	46.27	3.73	7%	28.27	21.73	43%	31.11	18.89	38%
47.26	2.74	5%	40.51	9.49	19%	43.38	6.62	13%	46.65	3.35	7%	29.18	20.82	42%	30.23	19.77	40%
47.49	2.51	5%	38.26	11.74	23%	42.73	7.27	15%	47.23	2.77	6%	27.40	22.60	45%	27.91	22.09	44%
48.03	1.97	4%	39.18	10.82	22%	45.47	4.53	9%	47.01	2.99	6%	27.42	22.58	45%	26.66	23.35	47%
48.03	1.97	4%	40.08	9.92	20%	43.58	6.42	13%	47.43	2.57	5%	29.05	20.95	42%	25.47	24.53	49%
48.38	1.62	3%	41.46	8.54	17%	45.53	4.47	9%	46.57	3.43	7%	28.52	21.48	43%	26.13	23.87	48%
49.21	0.79	2%	41.23	8.77	18%	46.62	3.38	7%	46.06	3.94	8%	29.14	20.86	42%	23.62	26.38	53%
48.85	1.15	2%	40.97	9.04	18%	48.12	1.88	4%	45.46	4.54	9%	27.98	22.02	44%	24.98	25.02	50%
49.70	0.30	1%	42.86	7.14	14%	44.81	5.19	10%	46.20	3.80	8%	27.28	22.72	45%	25.69	24.31	49%
49.14	0.86	2%	43.98	6.02	12%	44.78	5.22	10%	46.87	3.13	6%	29.37	20.63	41%	24.86	25.14	50%
49.85	0.15	0%	41.47	8.53	17%	44.26	5.74	11%	45.61	4.39	9%	28.69	21.31	43%	26.49	23.51	47%
49.17	0.83	2%	41.30	8.70	17%	46.13	3.87	8%	45.26	4.74	9%	29.20	20.80	42%	25.82	24.18	48%
49.88	0.12	0%	41.23	8.77	18%	46.21	3.79	8%	45.60	4.40	9%	29.21	20.79	42%	25.57	24.43	49%
48.70	1.30	3%	41.17	8.83	18%	46.75	3.25	7%	43.49	6.51	13%	29.18	20.82	42%	22.89	27.11	54%
48.61	1.39	3%	40.34	9.66	19%	47.80	2.20	4%	45.73	4.27	9%	29.18	20.82	42%	24.06	25.94	52%
48.65	1.35	3%	41.44	8.56	17%	44.55	5.45	11%	46.41	3.59	7%	29.47	20.53	41%	25.39	24.61	49%
	42.55 46.49 47.26 47.49 48.03 48.03 48.03 48.38 49.21 48.85 49.70 49.85 49.17 49.88 48.70 48.61	12.55 7.45 12.55 7.45 16.49 3.51 17.26 2.74 17.49 2.51 18.03 1.97 18.03 1.97 18.03 1.97 18.38 1.62 19.21 0.79 18.85 1.15 19.70 0.30 19.14 0.86 19.85 0.15 19.17 0.83 19.88 0.12 18.70 1.30 18.61 1.39	12.55 7.45 15% 16.49 3.51 7% 17.26 2.74 5% 17.49 2.51 5% 18.03 1.97 4% 18.03 1.97 4% 18.03 1.97 4% 18.03 1.97 4% 18.03 1.97 4% 18.03 1.97 2% 18.38 1.62 3% 19.21 0.79 2% 18.85 1.15 2% 19.70 0.30 1% 19.14 0.86 2% 19.85 0.15 0% 19.17 0.83 2% 19.88 0.12 0% 18.70 1.30 3%	12.55 7.45 15% 37.99 16.49 3.51 7% 42.41 17.26 2.74 5% 40.51 17.49 2.51 5% 38.26 18.03 1.97 4% 39.18 18.03 1.97 4% 39.18 18.03 1.97 4% 40.08 18.38 1.62 3% 41.46 19.21 0.79 2% 41.23 18.85 1.15 2% 40.97 19.70 0.30 1% 42.86 19.14 0.86 2% 43.98 19.85 0.15 0% 41.47 19.17 0.83 2% 41.30 19.88 0.12 0% 41.23 18.70 1.30 3% 41.17 18.61 1.39 3% 40.34	12.55 7.45 $15%$ 37.99 12.01 16.49 3.51 $7%$ 42.41 7.59 17.26 2.74 $5%$ 40.51 9.49 17.49 2.51 $5%$ 38.26 11.74 18.03 1.97 $4%$ 39.18 10.82 18.03 1.97 $4%$ 39.18 10.82 18.03 1.97 $4%$ 40.08 9.92 18.38 1.62 $3%$ 41.46 8.54 19.21 0.79 $2%$ 41.23 8.77 18.85 1.15 $2%$ 40.97 9.04 19.70 0.30 $1%$ 42.86 7.14 19.14 0.86 $2%$ 43.98 6.02 9.85 0.15 $0%$ 41.47 8.53 9.17 0.83 $2%$ 41.30 8.70 19.88 0.12 $0%$ 41.23 8.77 18.70 1.30 $3%$ 40.34 9.66 18.61 1.39 $3%$ 40.34 9.66	12.55 7.45 $15%$ 37.99 12.01 $24%$ 16.49 3.51 $7%$ 42.41 7.59 $15%$ 17.26 2.74 $5%$ 40.51 9.49 $19%$ 17.49 2.51 $5%$ 38.26 11.74 $23%$ 18.03 1.97 $4%$ 39.18 10.82 $22%$ 18.03 1.97 $4%$ 40.08 9.92 $20%$ 18.38 1.62 $3%$ 41.46 8.54 $17%$ 19.21 0.79 $2%$ 41.23 8.77 $18%$ 19.70 0.30 $1%$ 42.86 7.14 $14%$ 19.70 0.30 $1%$ 42.86 7.14 $14%$ 19.70 0.30 $1%$ 42.86 7.14 $14%$ 19.14 0.86 $2%$ 43.98 6.02 $12%$ 9.85 0.15 $0%$ 41.47 8.53 $17%$ 9.17 0.83 $2%$ 41.30 8.70 $1.7%$ 18.70 1.30 $3%$ 41.17 8.83 $18%$ 8.61 1.39 $3%$ 40.34 9.66 $19%$	12.55 7.45 $15%$ 37.99 12.01 $24%$ 40.36 16.49 3.51 $7%$ 42.41 7.59 $15%$ 42.34 17.26 2.74 $5%$ 40.51 9.49 $19%$ 43.38 17.49 2.51 $5%$ 38.26 11.74 $23%$ 42.73 18.03 1.97 $4%$ 39.18 10.82 $22%$ 45.47 18.03 1.97 $4%$ 39.18 10.82 $22%$ 45.47 18.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 18.38 1.62 $3%$ 41.46 8.54 $17%$ 45.53 19.21 0.79 $2%$ 41.23 8.77 $18%$ 46.62 18.85 1.15 $2%$ 40.97 9.04 $18%$ 48.12 19.70 0.30 $1%$ 42.86 7.14 $14%$ 44.81 19.14 0.86 $2%$ 43.98 6.02 $12%$ 44.78 9.85 0.15 $0%$ 41.47 8.53 $17%$ 46.13 19.88 0.12 $0%$ 41.23 8.77 $18%$ 46.21 18.70 1.30 $3%$ 40.34 9.66 $19%$ 47.80 18.61 1.39 $3%$ 40.34 9.66 $19%$ 47.80	12.55 7.45 $15%$ 37.99 12.01 $24%$ 40.36 9.64 16.49 3.51 $7%$ 42.41 7.59 $15%$ 42.34 7.66 17.26 2.74 $5%$ 40.51 9.49 $19%$ 43.38 6.62 17.49 2.51 $5%$ 38.26 11.74 $23%$ 42.73 7.27 18.03 1.97 $4%$ 39.18 10.82 $22%$ 45.47 4.53 18.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 6.42 18.38 1.62 $3%$ 41.46 8.54 $17%$ 45.53 4.47 19.21 0.79 $2%$ 41.23 8.77 $18%$ 46.62 3.38 18.85 1.15 $2%$ 40.97 9.04 $18%$ 48.12 1.88 19.70 0.30 $1%$ 42.86 7.14 $14%$ 44.81 5.19 19.14 0.86 $2%$ 43.98 6.02 $12%$ 44.78 5.22 9.85 0.15 $0%$ 41.47 8.53 $17%$ 44.26 5.74 9.17 0.83 $2%$ 41.30 8.70 $17%$ 46.13 3.87 9.88 0.12 $0%$ 41.23 8.77 $18%$ 46.75 3.25 8.61 1.39 $3%$ 40.34 9.66 $19%$ 47.80 2.20 8.65 1.25 $2%$ 41.44 41.44 47.80 $2.$	12.55 7.45 $15%$ 37.99 12.01 $24%$ 40.36 9.64 $19%$ 46.49 3.51 $7%$ 42.41 7.59 $15%$ 42.34 7.66 $15%$ 47.26 2.74 $5%$ 40.51 9.49 $19%$ 43.38 6.62 $13%$ 47.49 2.51 $5%$ 38.26 11.74 $23%$ 42.73 7.27 $15%$ 48.03 1.97 $4%$ 39.18 10.82 $22%$ 45.47 4.53 $9%$ 48.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 6.42 $13%$ 48.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 6.42 $13%$ 48.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 6.42 $13%$ 48.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 6.42 $13%$ 48.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 6.42 $13%$ 48.03 1.62 $3%$ 41.46 8.54 $17%$ 45.53 4.47 $9%$ 49.21 0.79 $2%$ 41.23 8.77 $18%$ 46.62 3.38 $7%$ 49.70 0.30 $1%$ 42.86 7.14 $14%$ 44.78 5.22 $10%$ 49.70 0.86 $2%$ 43.98 6.02 $12%$ 44.78 5.22 $10%$ 49.85 0.12 <td>12.55$7.45$$15%$$37.99$$12.01$$24%$$40.36$$9.64$$19%$$41.85$$16.49$$3.51$$7%$$42.41$$7.59$$15%$$42.34$$7.66$$15%$$46.27$$17.26$$2.74$$5%$$40.51$$9.49$$19%$$43.38$$6.62$$13%$$46.65$$17.49$$2.51$$5%$$38.26$$11.74$$23%$$42.73$$7.27$$15%$$47.23$$18.03$$1.97$$4%$$39.18$$10.82$$22%$$45.47$$4.53$$9%$$47.01$$18.03$$1.97$$4%$$40.08$$9.92$$20%$$43.58$$6.42$$13%$$47.43$$18.03$$1.97$$4%$$40.08$$9.92$$20%$$43.58$$6.42$$13%$$47.43$$18.03$$1.97$$4%$$40.08$$9.92$$20%$$43.58$$6.42$$13%$$47.43$$18.03$$1.97$$4%$$40.08$$9.92$$20%$$43.58$$6.42$$13%$$47.43$$18.03$$1.97$$4%$$40.08$$9.92$$20%$$43.58$$6.42$$13%$$47.43$$18.03$$1.62$$3%$$41.46$$8.54$$17%$$45.53$$4.47$$9%$$46.57$$19.21$$0.79$$2%$$41.23$$8.77$$18%$$46.62$$3.38$$7%$$46.06$$18.85$$1.15$$2%$$43.98$$6.02$$12%$$44.78$$5.22$</td> 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7.45 $15%$ 37.99 12.01 $24%$ 40.36 9.64 $19%$ 41.85 16.49 3.51 $7%$ 42.41 7.59 $15%$ 42.34 7.66 $15%$ 46.27 17.26 2.74 $5%$ 40.51 9.49 $19%$ 43.38 6.62 $13%$ 46.65 17.49 2.51 $5%$ 38.26 11.74 $23%$ 42.73 7.27 $15%$ 47.23 18.03 1.97 $4%$ 39.18 10.82 $22%$ 45.47 4.53 $9%$ 47.01 18.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 6.42 $13%$ 47.43 18.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 6.42 $13%$ 47.43 18.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 6.42 $13%$ 47.43 18.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 6.42 $13%$ 47.43 18.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 6.42 $13%$ 47.43 18.03 1.62 $3%$ 41.46 8.54 $17%$ 45.53 4.47 $9%$ 46.57 19.21 0.79 $2%$ 41.23 8.77 $18%$ 46.62 3.38 $7%$ 46.06 18.85 1.15 $2%$ 43.98 6.02 $12%$ 44.78 5.22	12.55 7.45 $15%$ 37.99 12.01 $24%$ 40.36 9.64 $19%$ 41.85 8.15 1649 3.51 $7%$ 42.41 7.59 $15%$ 42.34 7.66 $15%$ 46.27 3.73 17.26 2.74 $5%$ 40.51 9.49 $19%$ 43.38 6.62 $13%$ 46.65 3.35 17.49 2.51 $5%$ 38.26 11.74 $23%$ 42.73 7.27 $15%$ 47.23 2.77 18.03 1.97 $4%$ 39.18 10.82 $22%$ 45.47 4.53 $9%$ 47.01 2.99 18.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 6.42 $13%$ 47.43 2.57 18.83 1.62 $3%$ 41.46 8.54 $17%$ 45.53 4.47 $9%$ 46.57 3.43 9.21 0.79 $2%$ 41.23 8.77 $18%$ 46.62 3.38 $7%$ 46.06 3.94 8.85 1.15 $2%$ 40.97 9.04 $18%$ 48.12 1.88 $4%$ 45.46 4.54 9.70 0.30 $1%$ 42.86 7.14 $14%$ 44.81 5.19 $10%$ 46.20 3.80 9.14 0.86 $2%$ 43.98 6.02 $12%$ 44.78 5.22 $10%$ 46.87 3.13 9.85 0.15 $0%$ 41.47 8.53 $17%$ 46.13 3.87	12.55 7.45 $15%$ 37.99 12.01 $24%$ 40.36 9.64 $19%$ 41.85 8.15 $16%$ 16.49 3.51 $7%$ 42.41 7.59 $15%$ 42.34 7.66 $15%$ 46.27 3.73 $7%$ 17.26 2.74 $5%$ 40.51 9.49 $19%$ 43.38 6.62 $13%$ 46.65 3.35 $7%$ 17.26 2.74 $5%$ 40.51 9.49 $19%$ 43.38 6.62 $13%$ 46.65 3.35 $7%$ 17.49 2.51 $5%$ 38.26 11.74 $23%$ 42.73 7.27 $15%$ 47.23 2.77 $6%$ 18.03 1.97 $4%$ 39.18 10.82 $22%$ 45.47 4.53 $9%$ 47.01 2.99 $6%$ 18.03 1.97 $4%$ 40.08 9.92 $20%$ 43.58 6.42 $13%$ 47.43 2.57 $5%$ 18.38 1.62 $3%$ 41.46 8.54 $17%$ 45.53 4.47 $9%$ 46.57 3.43 $7%$ 19.21 0.79 $2%$ 41.23 8.77 $18%$ 46.62 3.38 $7%$ 46.06 3.94 $8%$ 19.70 0.30 $1%$ 42.86 7.14 $14%$ 44.81 5.19 $10%$ 46.87 3.13 $6%$ 9.85 0.15 $0%$ 41.47 8.53 $17%$ 44.26 5.74 $11%$ 45.61 4.39 </td <td>12.55$7.45$$15%$$37.99$$12.01$$24%$$40.36$$9.64$$19%$$41.85$$8.15$$16%$$29.43$$16.49$$3.51$$7%$$42.41$$7.59$$15%$$42.34$$7.66$$15%$$46.27$$3.73$$7%$$28.27$$77.26$$2.74$$5%$$40.51$$9.49$$19%$$43.38$$6.62$$13%$$46.65$$3.35$$7%$$29.18$$77.49$$2.51$$5%$$38.26$$11.74$$23%$$42.73$$7.27$$15%$$47.23$$2.77$$6%$$27.40$$8.03$$1.97$$4%$$39.18$$10.82$$22%$$45.47$$4.53$$9%$$47.01$$2.99$$6%$$27.42$$8.03$$1.97$$4%$$40.08$$9.92$$20%$$43.58$$6.42$$13%$$47.43$$2.57$$5%$$29.05$$8.38$$1.62$$3%$$41.46$$8.54$$17%$$45.53$$4.47$$9%$$46.57$$3.43$$7%$$28.52$$99.21$$0.79$$2%$$41.23$$8.77$$18%$$46.62$$3.38$$7%$$46.06$$3.94$$8%$$29.14$$8.85$$1.15$$2%$$40.97$$9.04$$18%$$48.12$$1.88$$4%$$45.46$$4.54$$9%$$27.98$$9.70$$0.30$$1%$$42.86$$7.14$$14%$$44.31$$5.19$$10%$$46.87$$3.13$$6%$$29.37$$9.$</td> <td>12.55$7.45$$15%$$37.99$$12.01$$24%$$40.36$$9.64$$19%$$41.85$$8.15$$16%$$29.43$$20.57$$16.49$$3.51$$7%$$42.41$$7.59$$15%$$42.34$$7.66$$15%$$46.27$$3.73$$7%$$28.27$$21.73$$17.26$$2.74$$5%$$40.51$$9.49$$19%$$43.38$$6.62$$13%$$46.65$$3.35$$7%$$29.18$$20.82$$17.49$$2.51$$5%$$38.26$$11.74$$23%$$42.73$$7.27$$15%$$47.23$$2.77$$6%$$27.42$$22.60$$8.03$$1.97$$4%$$39.18$$10.82$$22%$$45.47$$4.53$$9%$$47.01$$2.99$$6%$$27.42$$22.58$$8.03$$1.97$$4%$$40.08$$9.92$$20%$$43.58$$6.42$$13%$$47.43$$2.57$$5%$$29.05$$20.95$$8.83$$1.62$$3%$$41.46$$8.54$$17%$$45.53$$4.47$$9%$$46.57$$3.43$$7%$$28.52$$21.48$$921$$0.79$$2%$$41.23$$8.77$$18%$$46.62$$3.38$$7%$$46.06$$3.94$$8%$$29.14$$20.86$$885$$1.15$$2%$$40.97$$9.04$$18%$$48.12$$1.88$$4%$$45.46$$4.54$$9%$$27.98$$22.02$$9.70$$0.30$$1%$$42.86$$7.14$</td> <td>2.55$7.45$$15%$$37.99$$12.01$$24%$$40.36$$9.64$$19%$$41.85$$8.15$$16%$$29.43$$20.57$$41%$$42.55$$7.45$$17%$$42.41$$7.59$$15%$$42.34$$7.66$$15%$$46.27$$3.73$$7%$$28.27$$21.73$$43%$$47.26$$2.74$$5%$$40.51$$9.49$$19%$$43.38$$6.62$$13%$$46.65$$3.35$$7%$$29.18$$20.82$$42%$$47.49$$2.51$$5%$$38.26$$11.74$$23%$$42.73$$7.27$$15%$$47.23$$2.77$$6%$$27.40$$22.60$$45%$$8.03$$1.97$$4%$$39.18$$10.82$$22%$$45.47$$4.53$$9%$$47.01$$2.99$$6%$$27.42$$22.58$$45%$$8.03$$1.97$$4%$$40.08$$9.92$$20%$$43.58$$6.42$$13%$$47.43$$2.57$$5%$$29.05$$20.95$$42%$$8.83$$1.62$$3%$$41.46$$8.54$$17%$$45.53$$4.47$$9%$$46.57$$3.43$$7%$$28.52$$21.48$$43%$$9.21$$0.79$$2%$$41.23$$8.77$$18%$$46.62$$3.38$$7%$$46.06$$3.94$$8%$$29.14$$20.86$$42%$$9.70$$0.30$$1%$$42.86$$7.14$$14%$$44.18$$5.19$$10%$$46.87$$3.13$$6%$</td> <td>$\begin{array}{cccccccccccccccccccccccccccccccccccc$</td> <td>$\begin{array}{cccccccccccccccccccccccccccccccccccc$</td>	12.55 7.45 $15%$ 37.99 12.01 $24%$ 40.36 9.64 $19%$ 41.85 8.15 $16%$ 29.43 16.49 3.51 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3.94 $8%$ 29.14 20.86 $42%$ 9.70 0.30 $1%$ 42.86 7.14 $14%$ 44.18 5.19 $10%$ 46.87 3.13 $6%$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

3%

47.57

2.43

5%

29.03

20.97

42%

25.31

24.69

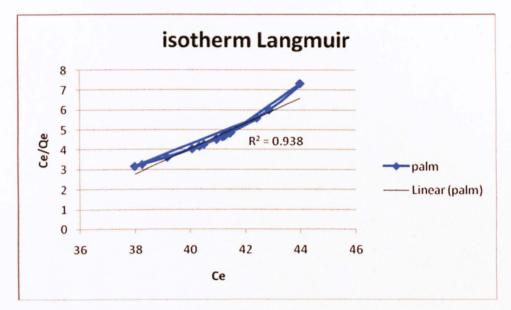
49%

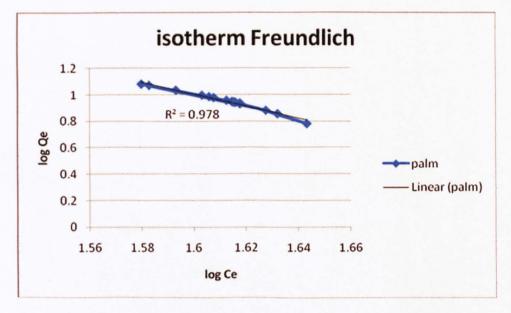
1.37

pressure

7.11. Isotherm Graph I

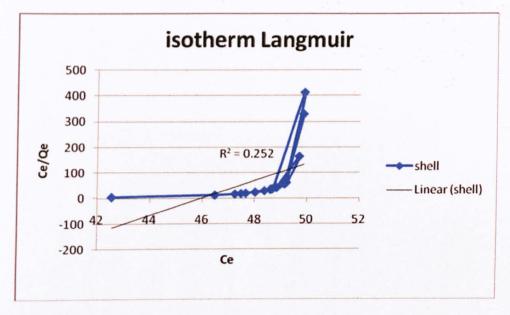
Adsorbent	: Burned palm trunk
Adsorbent mass	: 1 g/L
Adsorbent size	: 2 mm
pН	: 7
Nickel initial concentration	: 50 mg/L

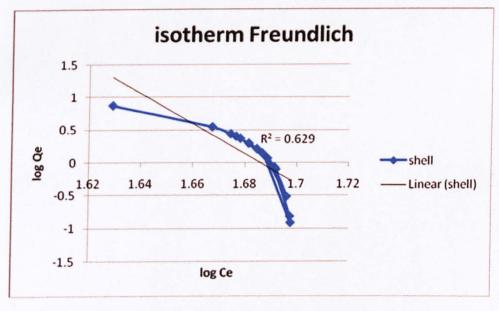




7.12. Isotherm Graph II

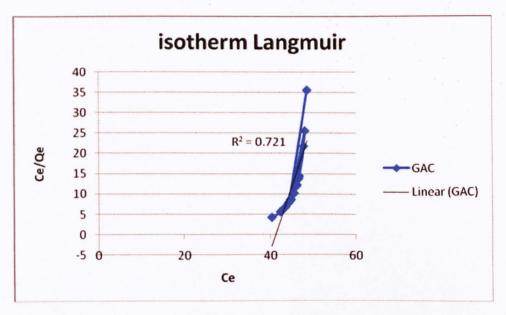
Adsorbent	: Cockle shell
Adsorbent mass	: 1 g/L
Adsorbent size	: 2 mm
pH	: 7
Nickel initial concentration	: 50 mg/L

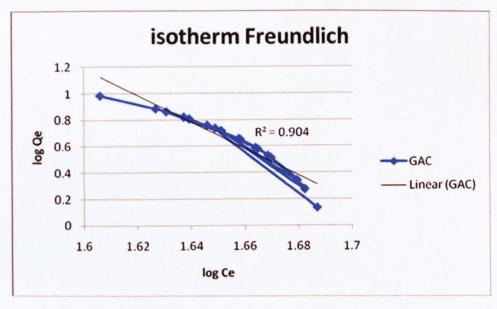




7.13. Isotherm Graph III

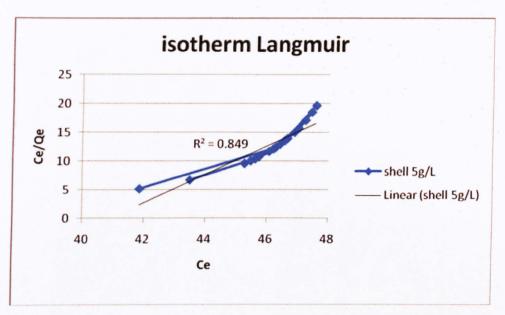
Adsorbent	: Granular activated carbon
Adsorbent mass	: 1 g/L
Adsorbent size	: 2 mm
pH	: 7
Nickel initial concentration	: 50 mg/L

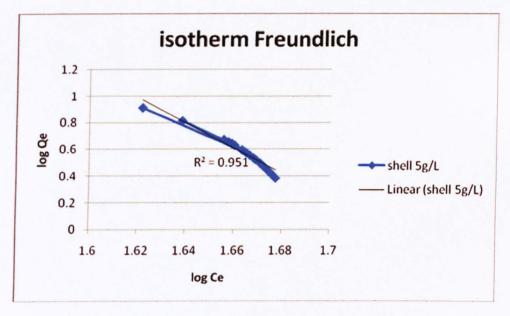




7.14. Isotherm Graph IV

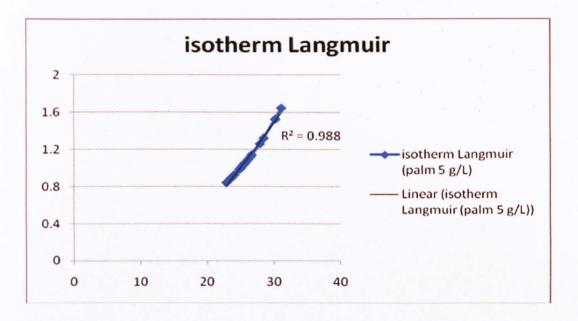
Adsorbent	: Cockle shell
Adsorbent mass	: 5 g/L
Adsorbent size	: 2 mm
pН	: 7
Nickel initial concentration	: 50 mg/L

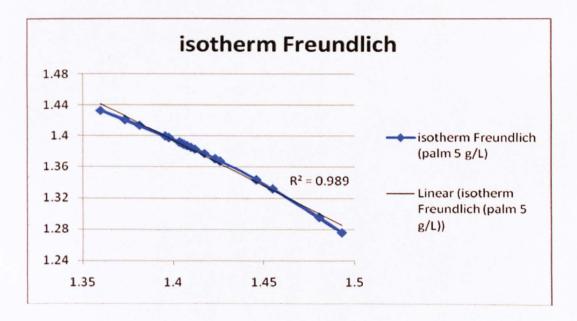




7.15. Isotherm Graph V

Adsorbent	: Burned palm trunk
Adsorbent mass	: 5 g/L
Adsorbent size	: 2 mm
pН	: 7
Nickel initial concentration	: 50 mg/L





7.16. Isotherm Graph VI

Adsorbent	: Burned palm trunk
Adsorbent mass	: 10 g/L
Adsorbent size	: 2 mm
pH	: 7
Nickel initial concentration	: 50 mg/L

