

**BIOSORPTION OF Ni(II) USING ALKALINE-TREATED RICE
HUSK**

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BIOSORPTION OF Ni(II) USING ALKALINE-TREATED RICE
HUSK

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ABSTRACT

Rice husk has been widely reported as a good sorbent for heavy metals. Alkaline-treated rice husk were used to investigate the potential of Ni(II) adsorption from synthetic solutions and wastewater in batch systems. Effects of operational variables such as pH, contact time, adsorbent dose, initial Ni(II) concentration were studied. Optimum Ni(II) adsorption was observed at pH 6. Experimental data showed increased amount of adsorbed Ni(II) with increasing adsorbent dose and decreased percent of adsorption with increasing initial Ni(II) concentration. The adsorption became constant after 40 min into the experiment. Biosorption mechanism of rice husk was analyzed using SEM, FTIR, ICP-OES and XRD. Langmuir adsorption isotherm was also studied to determine the respective constants and showed that the adsorption was favorable and the K_L was 0.292 L/mg. Results revealed that natural base could be used as efficient as synthetic bases for Ni(II) removal from wastewaters. Ni uptake from wastewater was not reduced to the parameter limit of effluent by the Environmental Quality (Industrial Effluent) Regulations 2009.

ABSTRAK

Sekam padi seringkali dilaporkan sebagai salah satu penyerap logam berat yang baik. Sekam yang telah dirawat oleh bes telah digunakan untuk mengkaji potensi penjerapan Ni(II) yang wujud di dalam larutan sintetik mahupun air sisa secara sistem kelompok. Kesan terhadap parameter-parameter fizikokimia seperti pH, tempoh penjerapan, dos penyerap juga dikaji. Data eksperimen melihat kandungan Ni(II) yang dijerap meningkat dengan peningkatan dos penyerap tetapi menurun jika kepekatan awal Ni(II) yang digunakan bertambah. Kadar penjerapan adalah malar selepas 40 minit. Proses penjerapan oleh sekam padi dianalisa melalui SEM, FTIR, ICP-OES, dan XRD. Isoterma Langmuir juga dikaji dan mendapati bahawa penjerapan adalah menggalakkan, di mana K_L adalah 0.292 L/mg. Hasil kajian menunjukkan bahawa bes semulajadi juga boleh menjerap Ni(II) dari air sisa secara berkesan malah beroleh hasil sebaik menggunakan bes sintetik. Pengurangan nikel yang berlaku dalam air sisa tidak mencecah piawaian yang ditetapkan dalam Peraturan-peraturan Kualiti Alam Sekitar (Efluen Industri) 2009.

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LIST OF SYMBOLS AND ABBREVIATIONS

ATSDR	Agency for Toxic Substances and Disease Registry
α	Alpha
Å	Angstrom, unit of length to measure wavelengths of light
BOD	Biological Oxygen Demand
Ca	Calcium
Ca(OH) ₂	Calcium Hydroxide
Cd	Cadmium
C ₆ H ₈ O ₇	Citric Acid
COD	Chemical Oxygen Demand
Cr	Chromium
°	Degree
DMG	Dimethylglycine
FTIR	Fourier Transform Infrared Spectroscopy
g/L	Gram Per Liter
h	Hour
HCl	Hydrochloric Acid
IARC	International Agency for Research on Cancer
Mg	Magnesium
µm	Micrometer
Mg/L	Milligram Per Liter
Min	Minute
NTP	National Toxicology Program
Ni	Nickel
NiSO ₄ ·6H ₂ O	Nickel Sulfate
HNO ₃	Nitric Acid
Ppm	Parts Per Million
%	Percent
K	Potassium

Rpm	Revolutions Per Minute
SEM	Scanning Electron Microscope
Na	Sodium
Na ₂ CO ₃	Sodium Carbonate
NaOH	Sodium Hydroxide
H ₂ SO ₄	Sulfuric Acid
TARH	Tartaric Acid-Modified Rice Husk
θ	Theta
TOC	Total Organic Carbon
v/v	Volume Per Volume Percent
WAXS	Wide-angle X-ray Scattering
XRD	X-ray Powder Diffraction

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CHAPTER 1. INTRODUCTION

1.1 Industrialization and Its Impacts

Industrialization has made a lot of positive impact to mankind until today, where we can see rapid growth of factories and industries to cater our needs for food, medications, mobility, and more. However, these conveniences have also brought drawbacks such as hazardous contamination and pollution. While benefitting from the advantages of industrialization, we also are exposed to excessive release of toxic materials from the factories, which can affect our immune and respiratory system on they enter our body due to their toxic, non-biodegradable, and bio-accumulative nature (Lam *et al.*, 2016). Similarly, plants and animals too will suffer if no precaution is made.

1.2 Heavy Metal Removal from Wastewater

There are various methods used by the factories as a mean to separate the metal ions from our water but they come with disadvantages, particularly the cost and the toxic sludge release. Due to this, researchers have discovered a cheaper yet efficient alternative called adsorption using natural resources or biosorption. Biosorption is defined as the removal of substances such as metal or metalloid species, compounds and particulates from solution by biological material or their products, especially bacteria, algae, yeast and fungi through physicochemical binding (Fanun, 2014). The main advantages of treating wastewater by means of adsorption are the reusability of biomaterial, low operating cost, improved selectivity for specific metal of interests, short operation time, and no production of secondary compounds which can be toxic.

1.3 Objectives

In this paper, the methods available for heavy metal treatment were studied as well as experimental variables that can affect nickel adsorption process. These variables could change the physicochemical attributes of the adsorbent and they include the pH, dose amount, contact time as well as initial concentration of nickel. Data obtained from the studies were further used in subsequent studies using synthetic wastewater and finally using industrial wastewater.

The experiment aimed to acquire the following objectives:

- i) Physical characterization of rice husk as biosorbent with the use of various alkaline pretreatment.
- ii) Optimization and kinetic study of the biosorption process variables for Ni(II) removal using various alkaline-treated rice husk.
- iii) Testing of optimized biosorption conditions for the industrial wastewater application.

1.4 Hypothesis

It was hypothesized that Ni(II) ions uptake in synthetic solution using alkaline-treated rice husk will be higher than using raw rice husk because the structure of the adsorbent has been modified, allowing more binding sites for adsorption.

CHAPTER 2. LITERATURE REVIEW

2.1. Background

Heavy metals like cadmium, zinc, copper, nickel, lead, mercury, and chromium have been widely exposed into the general population due to rapid industrialization and this situation poses a major global concern. These hazardous materials are often found in industrial wastewaters, which according to (Kadirvelu *et al.*, 2001; Williams *et al.*, 1998), originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries. Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders; therefore they must be removed before discharge.

2.2 Nickel and Its Importance in Industrialization

Nickel (Ni) is a very hard, silvery white metal that occurs naturally in soils and volcanic dust. According to the Nickel Institute (2017), nickel is used in a wide variety of industrial and consumer applications, with approximately 65% of the nickel produced going into the manufacture of stainless steels and 20% into other alloys specialized for uses such as aerospace and military applications. Alloy is produced through combination of nickel with other metals, which is then used for coins, stainless steel, and jewelry. In addition, some major applications of the nickel compounds used in the present study also include electroplating, electroforming, production of other basic metals and nickel salts, battery manufacturing, and as catalysts. During the process of nickel production, workers can be exposed to a variety of nickel compounds, ranging from very soluble to insoluble forms, as well as complex materials used or generated in the process (e.g., nickel ores, mattes and ash).

2.3 Routes of Nickel Exposure and Health Effects

The International Agency for Research on Cancer (IARC) classified metallic nickel in group 2B (possibly carcinogenic to humans) and nickel compounds in group 1 (carcinogenic to humans). It can be exposed through means of inhalation, oral, and dermal. Inhalation of this metal is predominant for nickel workers. On the other hand, nickel is distributed orally via ingestion of food as well as drinking water. Dermal exposure comes from nickel alloys and nickel-plated materials such as coins and jewelry. Nickel exposure may cause contact dermatitis according to the Agency for Toxic Substances and Disease Registry (2005). The National Toxicology Program (NTP) of the U.S. Department of Health and Human Services also reported a number of carcinogenicity studies performed in humans and animals, which indicates that nickel compounds cause cancer in human (Burwell, 2014). In addition, Borba *et al.* (2006) reported on serious lung and kidney problems, gastrointestinal distress and pulmonary fibrosis resulted by nickel exceeding its critical level.

2.4. Wastewater Treatments

According to Singh & Gadi (2012), metal ions are commonly treated from aqueous streams using reverse osmosis, electro dialysis, ultrafiltration, ion-exchange, chemical precipitation, and phytoremediation, which are explained in Table 2.1.

Based on the table, a few problems can be found, most of which require high cost and at the same time generate hazardous sludge. Hence the disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal have made it imperative for a cost-effective treatment method that is capable of removing heavy metals from aqueous effluents.

Table 2.1 Common procedures employed for heavy metal removal from wastewater effluent

Method	Description	Disadvantages
Reverse osmosis	Heavy metals separated by semi-permeable membrane at a greater-than osmotic pressure	Expensive
Electrodialysis	Heavy metals are separated through the use of semi-permeable ion-selective membranes. Electrical potential will be applied between two electrodes hence causes a migration of cations and anions towards respective electrodes	Metal hydroxides formation, which clog the membrane.
Ultrafiltration	Removal is done using porous membrane and application of pressure	Generates sludge
Ion-exchange	Exchange of ions held by electrostatic forces on the exchange resin with the heavy metal ions	Costly and results in partial removal of ions
Chemical precipitation	Addition of coagulants such as alum, lime, iron salts and other organic polymers to precipitate the metal ions	Generates large amount of sludge containing toxic
Phytoremediation	Use of certain plants to clean up contaminated water or soil	Time consuming

Source: (Ahalya *et al.*, 2003).

2.5. Biosorption as an alternative to treat heavy metal

Biosorption or adsorption is the ability of biological materials to accumulate heavy metals from wastewater through physicochemical pathways (Fourest & Roux, 1992) involving two phases; solid and liquid. The solid phase is also called the sorbent and is biological material whereas the liquid phase is the solvent, normally water, containing the sorbate, or the dissolved species for adsorption. The sorbate species will remain bound to the sorbent by several mechanisms because of higher affinity. The process continues until equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution (Ahalya *et al.*, 2003). The schematic mechanism of adsorption is shown in Figure 2.1 below.

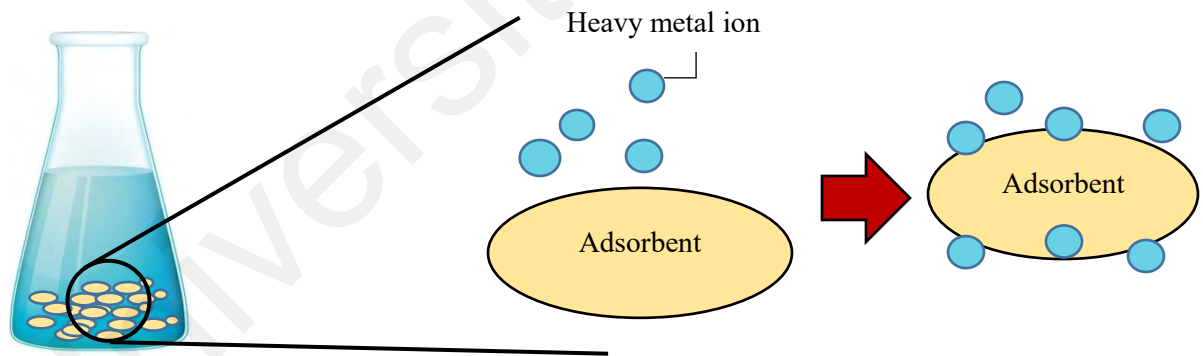


Figure 2.1. Heavy metal adsorption mechanism

Large number of studies on adsorption for heavy metal treatments suggest that adsorption is indeed effective to remove heavy metals from aqueous solutions. An adsorbent is only deemed low-cost if it is naturally abundant, is a byproduct of waste material from waste industry and it requires little or no processing for use (Bailey *et al.*, 1999). Biosorbents for removal of heavy metal ions mainly come under the following categories: bacteria, fungi, algae, industrial waste, agricultural wastes, and other polysaccharide materials (Torab-Mostaedi *et al.*, 2013).

Agroindustrial byproducts like plant wastes can be inexpensive as they have no or very low economic value. Furthermore, using plant wastes for wastewater treatment is feasible in a way as it uses simple technique, has good adsorption capacity, has selective adsorption of heavy metal ions, requires little processing and easy to regenerate. Several plant wastes such as papaya wood (Saeed *et al.*, 2005), maize leaf (Babarinde *et al.*, 2006), teak leaf powder (King *et al.*, 2006), lalang (*Imperata cylindrica*) leaf powder (Hanafiah *et al.*, 2007), rubber (*Hevea brasiliensis*) leaf powder (Hanafiah *et al.*, 2006), *Coriandrum sativum* (Karunasagar *et al.*, 2005), peanut hull pellets (Johnson *et al.*, 2002), sago waste (Quek *et al.*, 1998), saltbush (*Atriplex canescens*) leaves (Sawalha *et al.*, 2006), tree fern (Ho *et al.*, 2004), rice husk ash and neem bark (Bhattacharya *et al.*, 2006), grape stalk wastes (Villaescusa *et al.*, 2004) were used for adsorption purpose (Wan Ngah & Hanafiah, 2008).

Modification or treatment of plant wastes is usually performed before being applied for the decontamination of heavy metals. This is because several problems may arise from the application of untreated plant wastes such as low adsorption capacity, high chemical oxygen demand (COD) and biological oxygen demand (BOD) as well as total organic carbon (TOC) due to the release of soluble organic compounds that are in the plant materials (Gaballah *et al.*, 1997; Nakajima & Sakaguchi, 1990). The increase of the COD, BOD and

TOC can result in the depletion of oxygen content in water and henceforth threatens aquatic life.

2.6 Modification of plant wastes for adsorption

Prior to adsorption, the plant wastes can be modified first using chemicals. This pretreatment step will ensure that soluble organic compound is extracted and enhance adsorption capacity. The goal of pretreatment is therefore to modify plant cell wall physiochemical features such that the resulting biomass is more amenable for deconstruction (Sun *et al.*, 2014). According to Wan Ngah and Hanafiah (2008), pretreatment is done either using base solutions such as sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃), calcium hydroxide, Ca(OH)₂, acid solutions such as hydrochloric acid (HCl), nitric acid (HNO₃), citric acid (C₆H₈O₇), sulfuric acid (H₂SO₄), oxidizing agents for instance hydrogen peroxide, and also dyes.

According to Gaballah *et al.* (1997), the pretreatment of plant wastes can extract soluble organic compounds and enhance chelating efficiency. The proposed mechanism for adsorption after pretreatment consists of three steps namely (i) reaction between the metal ions and carboxylic groups of polysaccharides; (ii) hydrogen bonding of hydrated metal ions with cellulose; and (iii) formation of complexes with (OH) of the phenolic groups of lignin.

2.7. Using rice husk as a biosorbent

Rice husk or rice hull is a feasible sorbent of many metals such as nickel, cadmium, and chromium (Guo *et al.*, 2003; Nakbanpote *et al.*, 2002). 480,000 tonnes of rice husk are left behind annually as byproduct of rice production according the Malaysian Ministry of Agriculture. According to Rahman *et al.* (1997), rice husk is composed of cellulose (32.24%), hemicellulose (21.34%), lignin (21.44%) and mineral ash (15.05%). It also contains high

percentage of silica in its mineral ash, which is valued around 96.34% (Rahman & Ismail, 1993). Effects of pretreatment of rice husks include lignin and hemicellulose removal, cellulose crystallinity reduction and increasing of the surface area (Sun *et al.*, 2014).

In general, chemically modified or treated rice husk exhibited higher adsorption capacities on heavy metal ions than unmodified rice husk. Notable results using modified rice husk were achieved by a number of researches such as in the sorption of cadmium (Cd) (Kumar & Bandyopadhyay, 2006) and the sorption of cadmium and lead (Tarley *et al.*, 2004). The study also concluded that the adsorption capacity of cadmium was enhanced when the rice husk was treated with sodium hydroxide, sodium carbonate and epichlorohydrin. The treatment with base had removed any base-soluble materials on the rice husk surface that could interfere with its adsorption property. Likewise, Tarley *et al.* (2004) reported double increase of the adsorption of Cd when rice husk was treated with NaOH.

CHAPTER 3. METHODOLOGY

3.1. Preparation of adsorbent

Rice husk was obtained from a local paddy processing mill in the northern part of Malaysia. The collected husk was washed with deionized water a few times to remove impurities and then oven-dried at 60°C overnight. The resultant raw rice husk was preserved in an air-sealed bag until further use.

3.2 Alkaline pretreatment of adsorbent

The raw rice husk was treated with 1% (w/v) of bases (namely ash, urea, NaOH, CaCO₃) by soaking the husk in each alkaline solution for 4 h. The ash was the byproduct of an agroindustrial processing plant. Subsequently, the raw rice husk was washed thoroughly with deionized water until the pH was neutralized and then dried in an oven at 60°C overnight. Dried pretreated rice husk was then kept in air-sealed bag for storage until next use.

3.3 Adsorbent characterization techniques

3.3.1 Scanning Electron Microscopy (SEM) Analysis

The surface area analysis of each treated adsorbent was studied using SEM (JEOL JSM-70001F). Each pieces of rice husk corresponding to different method of pretreatment was mounted on adhesive tapes and then metallized with gold prior to microscopy test. All specimens were kept at room temperature. Images were taken at 500x magnification and 15.0 kV beam voltage. Micrographs were taken multiple times at different angles to ensure full coverage of the surface. The effect of pretreatment on the rice husk was studied by comparing the micrographs of untreated rice husk with treated samples.

3.3.2 X-Ray Diffraction (XRD) Analysis

XRD was used to yield information on the percentage crystallinity of the cellulose in order to distinguish difference between the pre-treated adsorbent (Rendle, 2003). The dimensional atomic structure of each adsorbent was characterized using XRD diffractometer (PANalytical) under the setting of 1.540Å wavelength ($K\alpha$) for 2θ range of (5-40) °.

3.3.3 Fourier Transform Infrared (FT-IR) Spectroscopy Analysis

Due to its sensitivity in detecting vibrational frequencies of bonds, FTIR was used to determine the functional groups within the adsorbents and keep track of the changes in the bonds strength before and after adsorption (Barth, 2007). The rice husk was evaluated using the FTIR (Perkin Elmer) by scanning at 4 cm^{-1} resolution in wavelengths of (450-4000) cm^{-1} at room temperature. Spectra were recorded

3.4. Preparation of Nickel (Ni) solutions

Analytical graded nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) was used in the preparation of synthetic nickel solution. Nickel standard stock solution (1mg/1ml) was prepared by dissolving nickel sulfate in deionized water. The nickel working stock solutions were also prepared in different concentrations between (0 - 0.5) mg/ml by diluting the standard stock solution with deionized water. The range was chosen as it was easy to prepare for further use in making serial solutions for the study.

3.5. Preparation of Ni standard curve and Ni concentration determination

A standard curve of nickel concentration in solution was made in order to determine the amount of Ni in the solution before and after treatment. A serial solutions of five nickel concentrations were prepared 0.01-0.25 (mg/ml) by diluting the standard stock solution. The amount of nickel in solution was determined spectrophotometrically using the dimethylglyoxime (DMG) method (Flores-Garnica *et al.*, 2013). The solution and materials used were of analytical grade. 1% (v/v) DMG solution was prepared by diluting it with 95% (v/v) ethanol and stored in amber bottle. 10% (w/v) sodium citrate solution and 2% (v/v) ammonium hydroxide (30%, Mallinckrodt) were also prepared. Absorbance of the brownish red color was measured at 450 nm at room temperature by spectrophotometer (Spectronic Spec 20D) within 30 min from when DMG was added to stop the reaction. The absorbance value was plotted against nickel concentration.

3.6. Studies of Ni adsorption by untreated rice husk under different physicochemical variables

Adsorption studies were carried out using a series of 250ml conical flasks containing 100ml of 100 ppm Ni(II) concentration. Effects of operational variables such as pH, contact time, adsorbent dose, and initial Ni(II) concentration were studied. Each parameter was performed in triplicates to prevent any inconsistency. The pH of the solution was adjusted accordingly with 0.1 N NaOH or HCl. The amount of adsorbent dose added ranged from (20-100) g/L. Ni(II) solutions were prepared at (20-100) ppm by dilution method. Flasks were agitated at a constant speed of 180rpm for each run. Samples were collected at different experimental times to study the effect of time. At the end of the adsorption, the solutions were centrifuged at 4000 rpm and the filtered through 0.2- μ m filter (Millipore). The

remaining filtrates were further analyzed for the determination of nickel as mentioned in Section 3.5.

3.7. Comparison study on adsorption using different alkaline-treated rice husk

Following optimization, another study was carried out to compare adsorption between different types of pretreatment materials. The adsorbent used had been pretreated beforehand with several bases. The condition for adsorption was pH 6, agitation speed of 180 rpm, and adsorbent dose of 4.0 g/L. Adsorption of nickel was done for 1 h to ensure concentration equilibrium. Another test was performed to observe the effect of pretreatment on the time taken to reach equilibrium by using the adsorbent with the highest adsorption (%) previously. The experimental values used were 100 ppm Ni at pH 6, stirring speed at 180 rpm and adsorbent dose of 4.0g/L.

3.8. Nickel adsorption in industrial wastewater sample

Biosorption was conducted at optimal conditions based on the results collected from Section 3.6 (pH 6, 180 rpm, 4.0 g/L adsorbent, 1 hr) using wastewater sample that was collected from the UEDA Plating factory based in the HICOM Industrial Estate, Shah Alam. The adsorbent of choice was based on the results from the study in Section 3.7, which took the pretreatment that showed the highest nickel reduction in the solution.

3.8.1. Wastewater analysis

Samples of untreated wastewater and treated were further analyzed for heavy metal ions concentration through ICP-EOS analysis by the Department of Geology, University of Malaya, Kuala Lumpur.

3.9 Statistical analyses

All statistical analyses including mean, standard error, and standard deviation were performed using Microsoft Office Excel. Kinetic studies were done to determine the reaction order of nickel adsorption whereas the Langmuir adsorption isotherm was used to determine the constants following adsorption experiments.

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CHAPTER 4. RESULTS AND DISCUSSION

4.1. Characterization of rice husk

To determine the morphological and physiochemical properties of rice husk, samples were analyzed using SEM, FTIR, and XRD. SEM images were captured at 500x magnification and shown in Figure 4.1. It is clearly shown that untreated rice husk retained its smooth surface composed of lignin, hemi-cellulose, and wax. All treated samples (B,C, D, E) however, had rough, exposed surface due to the effect of alkali pretreatment.

FTIR spectra (Figure 4.2) indicated peaks and bands that correspond to several functional groups, which are summarized in Table 4.1. The O-H groups were represented by the broad bands at around 3400 cm^{-1} . C-H stretch was shown by bands at $2900\text{-}2916\text{ cm}^{-1}$. The peaks at $1510\text{-}1650\text{ cm}^{-1}$ could indicate the presence of unsaturated group such as alkenes (Naiya *et al.*, 2011). Pre-treated rice husk seems to have its Si-O stretching at 1056 cm^{-1} shifted, indicating that the Si-O group could have participated in metal binding. The band representative of nonsymmetric glycosidic bonds C-O-C (Fan *et al.*, 2012) was shown by the peak at around 1160 cm^{-1} . The intensity of the bond was reduced as a result of alkaline pretreatment and indicated that the bonds were broken down in the process.

Data collected from XRD (Figure 4.3) was translated into the crystallinity information of the samples. XRD analysis was done under the WAXS method at angles between $(5\text{-}40)^\circ$. As rice husk consists mainly of crystalline (cellulose) and amorphous (hemicellulose, lignin) structures (Kumar *et al.*, 2010; Nazir *et al.*, 2013), the sharp intensity peak at $2\theta=22.4^\circ$ indicated cellulose whereas the amorphous peak was reflected by the high peak at $2\theta=16^\circ$. The high intensity peak suggests that the pretreatment had successfully depolymerized and delignified the rice husk.

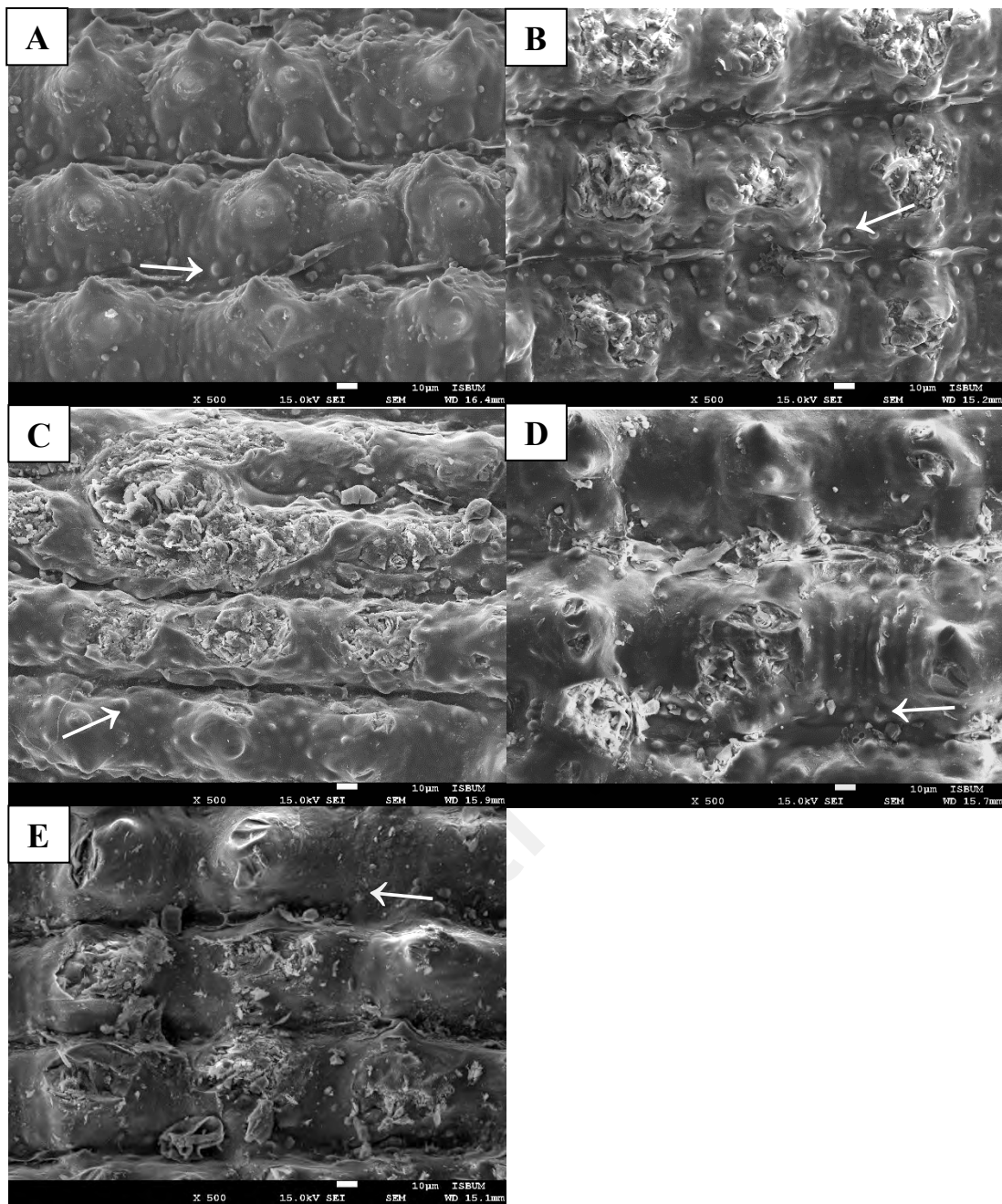


Figure 4.1. SEM micrographs of rice husk captured under 500x magnification after pre-treatment using different types of alkaline solution for 4 h, A) Control (Untreated); B) NaOH-treated; C) CaCO_3 -treated; D) Urea-treated; E) Ash-treated. Symbol: Arrow – Silica body.

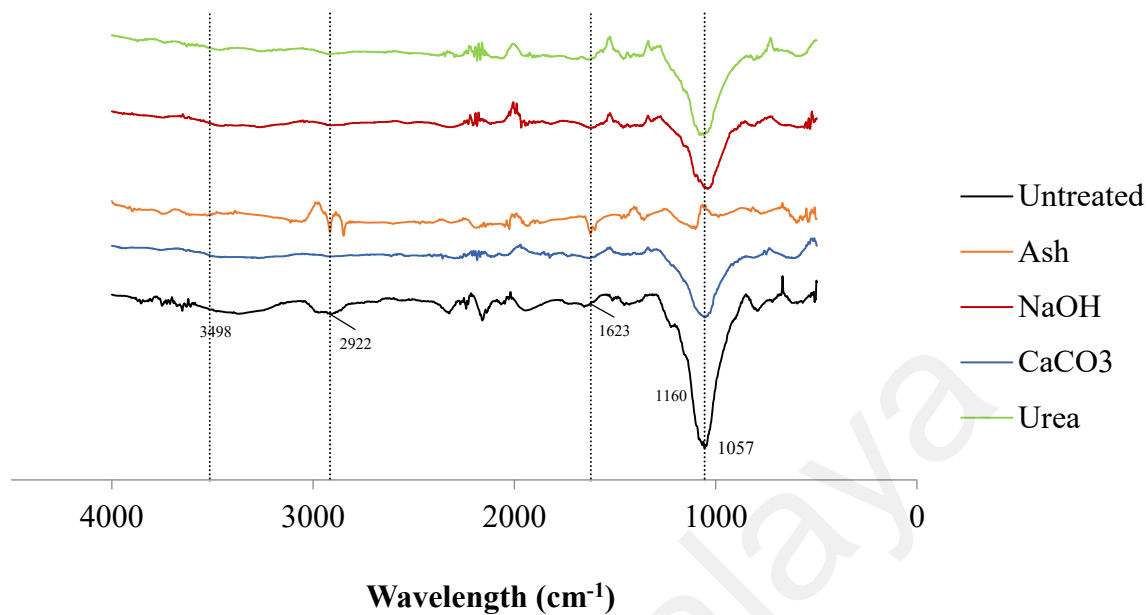


Figure 4.2. FTIR spectra of ground rice husk before and after pre-treatment.

Table 4.1 Infrared absorption frequencies of functional groups

Functional groups	Assignment	Absorption peaks (cm ⁻¹)
Alcohols	O-H stretch	3400
Alkanes	C-H stretch	2900-2916
Alkenes	C=C stretch	1510-1650
Ester bonds	C-O-C	1160
Organosilicon	Si-O stretch	1055

Note: Adapted from “Characteristic IR Band Positions” by the Lawrence Berkeley National Laboratory (2016). <http://infrared.als.lbl.gov/IRbands.html>

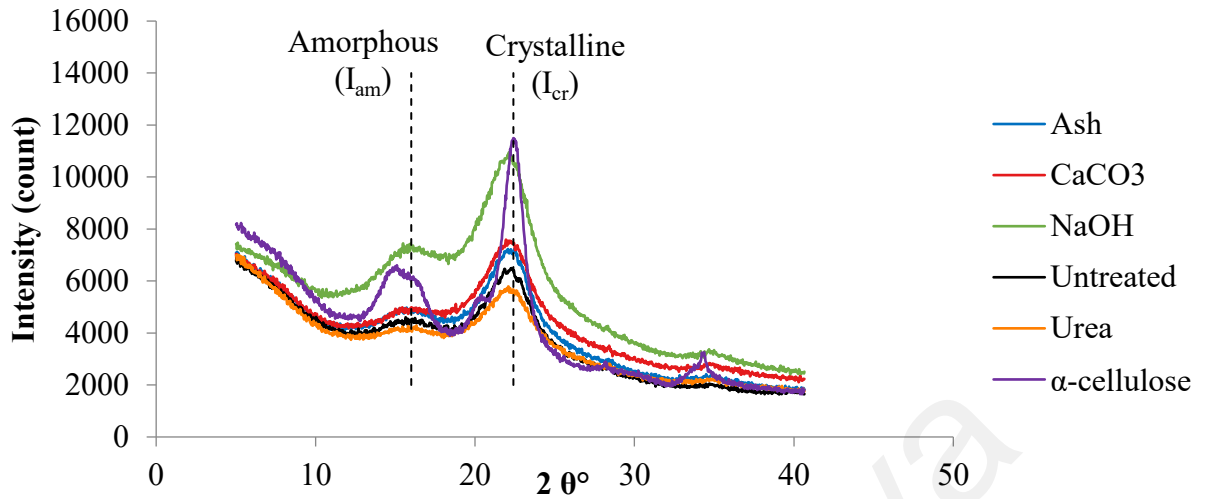


Figure 4.3. XRD patterns of rice husk before and after pretreatment with alkaline bases.

From the XRD patterns in Figure 4.3, the crystallinity index (*CrI*) of the specimens was determined from the following equation formulated by Segal’s method (Danial *et al.*, 2015):

$$CrI = \left(\frac{I_{cr} - I_{am}}{I_{cr}} \right) \times 100\% \dots\dots\dots(\text{Equation 1})$$

where I_{cr} represents the highest diffraction peak corresponding to the crystalline structure of the sample, I_{am} denotes the lowest diffraction peak of the amorphous background. Table 4.2 lists the *CrI* of the untreated and pretreated rice husk.

Table 4.2 Crystallinity index of rice husk samples pretreated by various kinds of alkaline solution

Samples	I_{cr} (°)	I_{am} (°)	<i>CrI</i> (%)
Ash	22.5	16.3	31.3
CaCO ₃	21.9	16.3	34.6
NaOH	22.1	16.0	32.1
Untreated RH	22.3	16.2	29.7
Urea	22.1	16.3	26.1
α-cellulose (Control)	22.4	15.9	45.4

4.2. Nickel removal from aqueous solution

4.2.1. Nickel standard curve

A standard curve of nickel concentration in solution was made in order to determine the amount of Ni in the solution before and after treatment. The standard curve was done without following the existing standard curves made by previous studies because different concentration of nickel solution was used in this study. By using the DMG method, absorbance at 450nm versus nickel concentration in mg/ml was plotted (Figure 4.4). DMG was chosen for the colorimetric approach to determine nickel because it could form a nickelic dimethylglyoxime complex in a weak ammoniacal solution. The graph in Figure 4.4 showed an increase of absorbance as the nickel concentration increased.

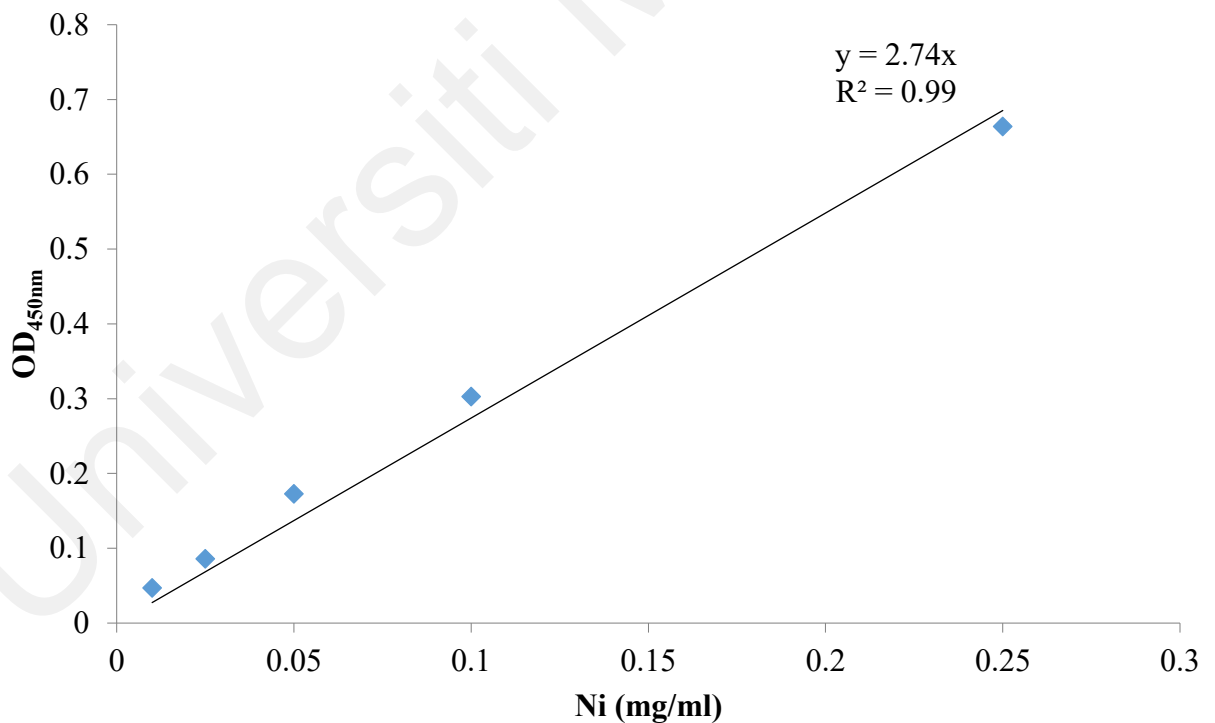


Figure 4.4. Nickel standard curve

4.2.2. *Effect of physicochemical properties on nickel reduction*

Experiments were performed using untreated rice husk to study the relationship between experimental variables (pH, contact time, nickel concentration, adsorbent dose) and nickel reduction. Findings were reported and discussed in Sections 4.2.2.1 – 4.2.2.4.

4.2.2.1. *Effect of pH*

Figure 4.5 demonstrates the influence of solution pH on the adsorption of nickel onto rice husk. The results showed that Ni(II) sorption was increasing as the acidity decreased and reduction was optimum when the pH of the solution was 6. For this reason, pH 6 was used in subsequent studies. As seen in Figure 4.5, the optimum pH for Ni(II) adsorption with untreated rice husk was at pH 6.

According to Malkoc & Nuhoglu (2005), the adsorption of heavy metal is critically linked with pH. In general, untreated biomass is found to contain light metal ions such as K^+ , Na^+ , Ca^{2+} , and Mg^{2+} (Malkoc & Nuhoglu, 2005). Chemical alterations reacted to displace the light metal ions from the binding sites, allowing for the occupation of selected ion on the biomass.

In this experiment, the pH values were limited to 7 because it was observed that at higher pH, nickel precipitation as $Ni(OH)_2$ is likely to occur (Lee & Lee, 2005). Therefore, studies were only performed at pH below 8 to restrict for only adsorption to take place instead of a combined occurrence between biosorption and precipitation, which would be predominated by $Ni(OH)_2$ precipitation. Similarly, Wong *et al.* (2003) reported that the optimum pH for adsorption of copper and lead tartaric acid modified rice husk (TARH) were 5.2 and 5.3 respectively, which are not too different from nickel adsorption. The pH chosen

would also be different if another type of adsorbent is used such as pH 4.0 for tea waste (Malkoc & Nuhoglu, 2005) and pH of 12 for paper mill effluent (Rajalakshmi *et al.*, 2009).

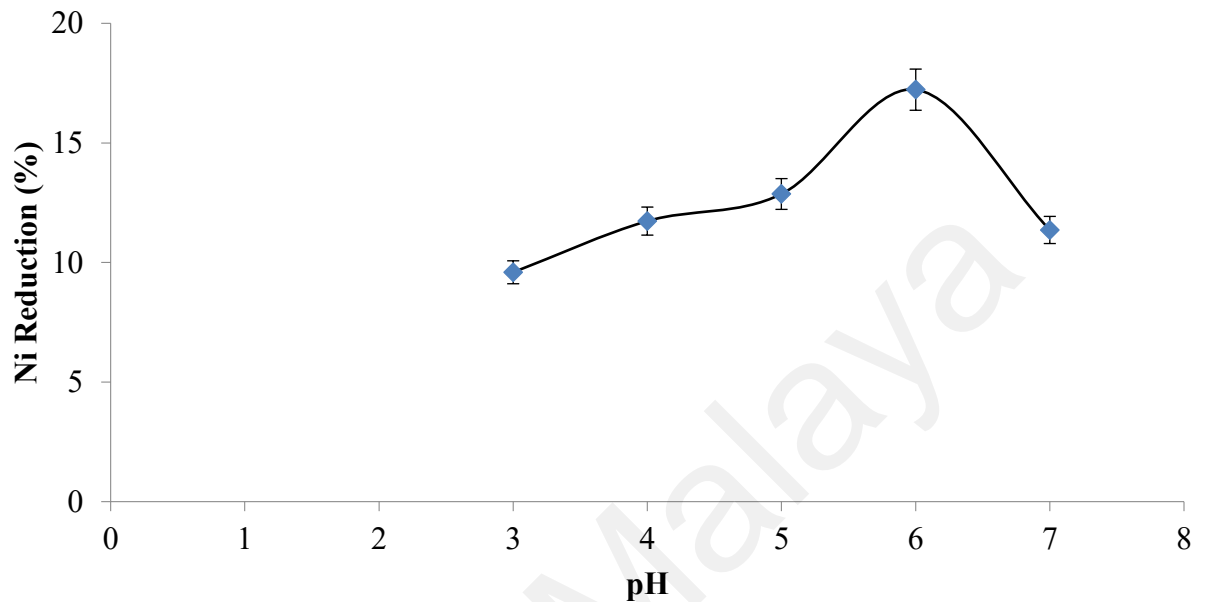


Figure 4.5. Effect of solution pH on nickel sorption capacity by rice husk

4.2.2.2. Effect of contact time

The effect of contact time between the adsorbent rice husk with nickel solution was studied to ensure that equilibrium was achieved, thus indicating maximal nickel sorption. The condition for adsorption was using 100 ppm nickel solution at pH 6, shaking speed at 180 rpm, and adsorbent dose of 4.0g/L. The result in Figure 4.6 shows that nickel reduction was taking place after 20 min into adsorption test and went stationary after 60 min. This means that further adsorption beyond this point will incur no addition to nickel reduction due to equilibrium between nickel ions in the solution and the adsorbent. Similarly, this pattern of equilibrium was also observed in the studies by Wong *et al.* (2003), where the uptake of Cu and Pb was rapid in the first 60 mins. Also, the process began to remain stagnant after around 120 mins.

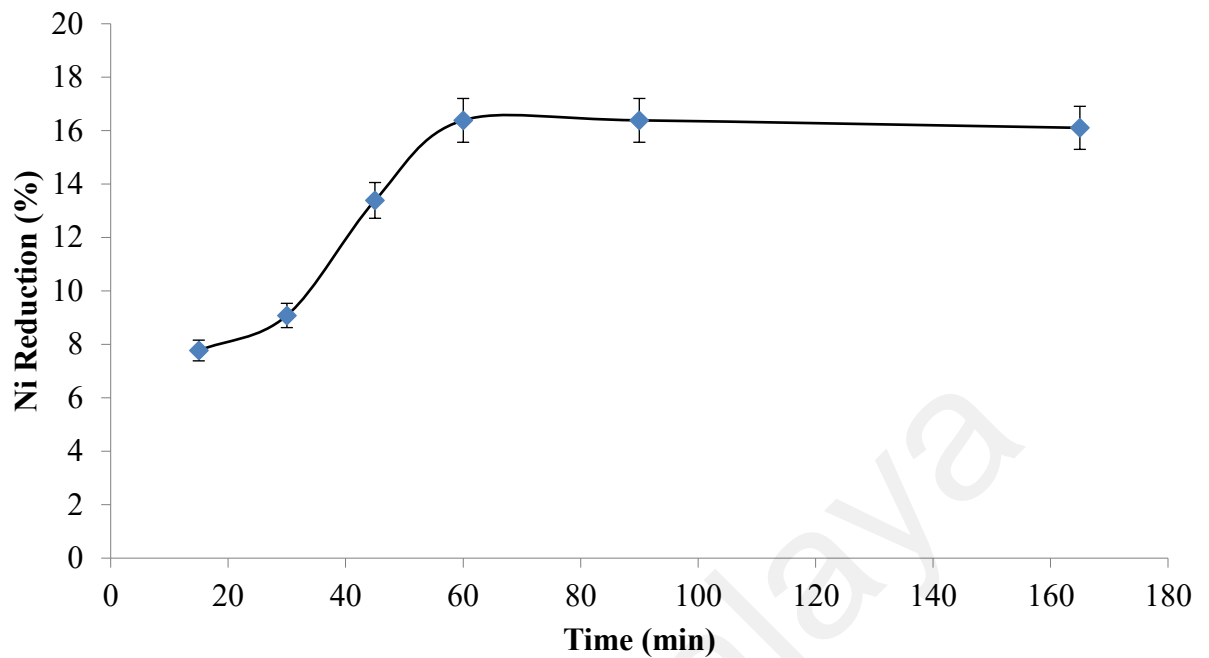


Figure 4.6. Effect of contact time between rice husk and nickel solution on the percent of nickel reduction after 3 h.

4.2.2.3. *Effect of initial nickel concentration*

To study the effect of initial nickel concentration in the solution on Ni reduction, the adsorption was done using 100 ppm Ni at pH 6, shaking speed at 180 rpm, and 4.0g/L adsorbent dose. Based on the result reflected by Figure 4.7, nickel reduction was the highest when initial nickel concentration used was 20 ppm. It also showed that nickel reduction became less effective as the initial nickel concentration was increased. The result could have been due to the ratio of available surface to the initial Ni(II) concentration was larger when the concentration is small hence higher removal of nickel, whereas the ratio was lower in the case of higher initial nickel concentration.

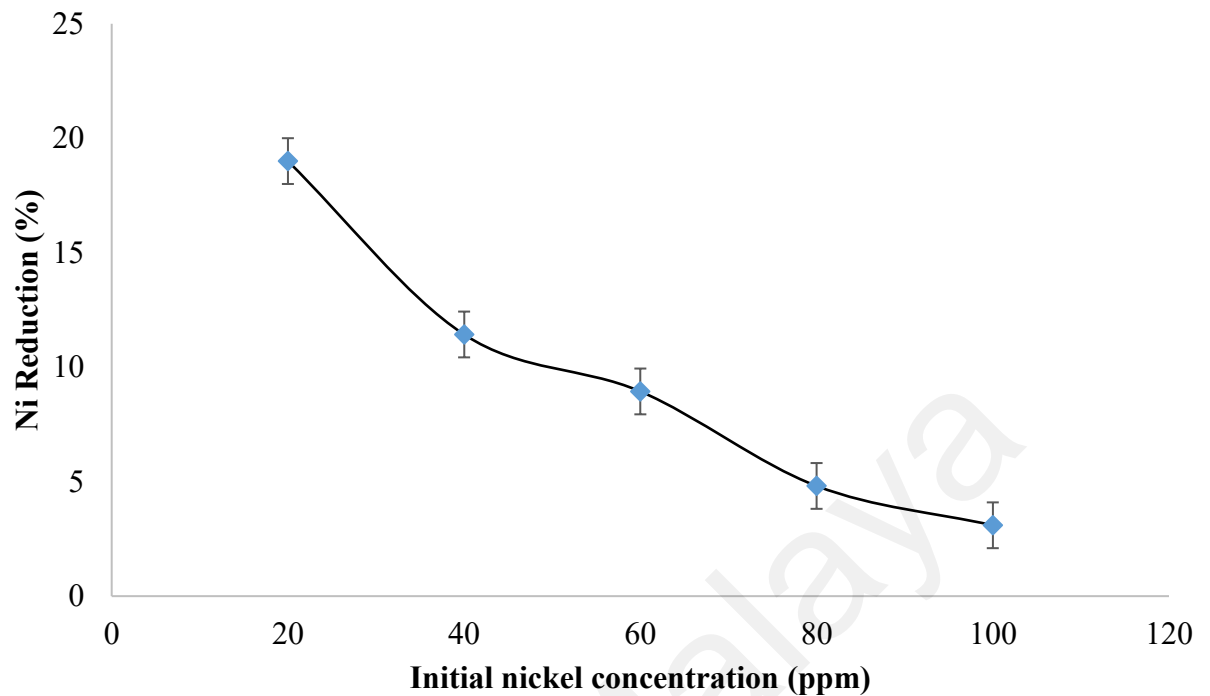


Figure 4.7. Effect of initial nickel concentration on nickel reduction after 3-hour treatment.

4.2.2.4. *Effect of adsorbent dose*

A study on the effect of adsorbent dose toward nickel reduction was also conducted at pH 6, 180 rpm agitation speed, and 100 ppm initial nickel concentration. Based on the experiment, the results in Figure 4.8 showed that the adsorbent dose was directly affecting the percent of nickel reduction. This observation signifies that as more adsorbent were added, there were binding sites for the nickel ions to adsorb to. Similar findings were reported when using activated rice husk carbon, activated alumina, and tea waste as adsorbents to remove nickel (Bishnoi *et al.*, 2004; Malkoc & Nuhoglu, 2005).

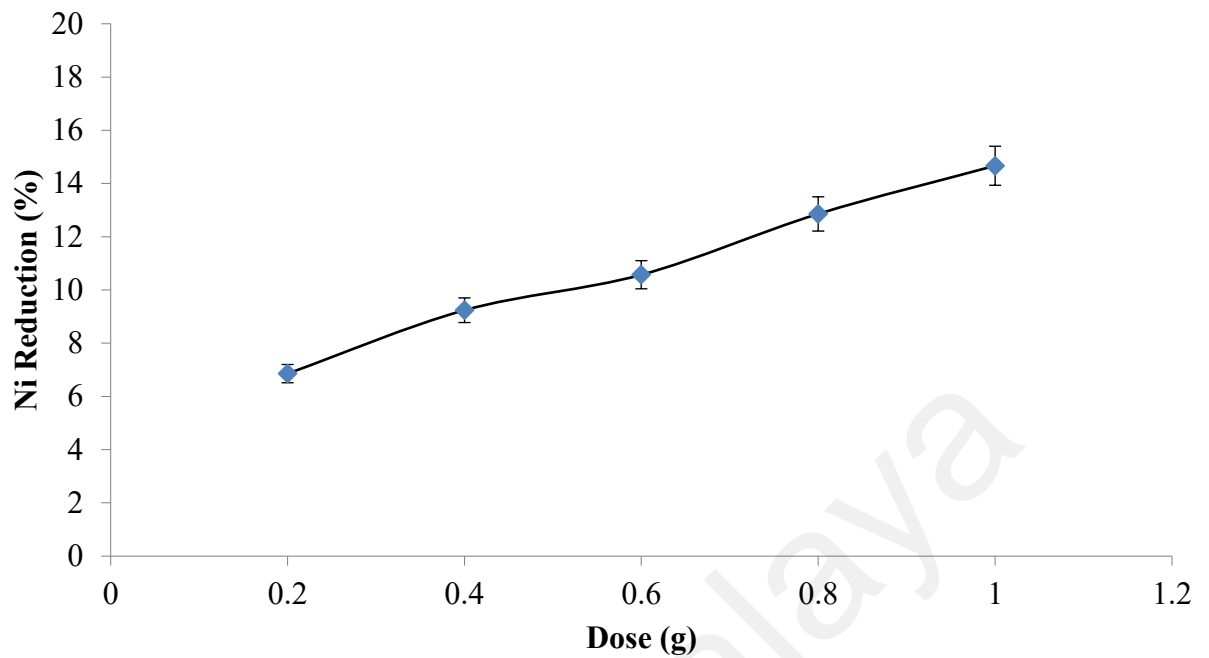


Figure 4.8. Effect of adsorbent dose on nickel reduction after 3-hour treatment.

4.3. Evaluation of nickel adsorption using pretreated rice husk under optimized parameters

Different natural and commercial bases were employed in the pretreatment step for this experiment. To examine the efficiency of the bases, percent of nickel reduction for each base were recorded. The study was performed using 100 ppm nickel solution at pH 6, 4.0 g/L adsorbent dose, agitation speed of 180 rpm for 1 h. The results in Figure 4.9 showed that ash treated rice husk had given the most percent in nickel reduction at 46.90% due to removal of most of the unwanted structures in adsorption at high pH level. Thus, ash could be a feasible material for use in pretreatment because it is readily available after incineration of agroindustrial biomass.

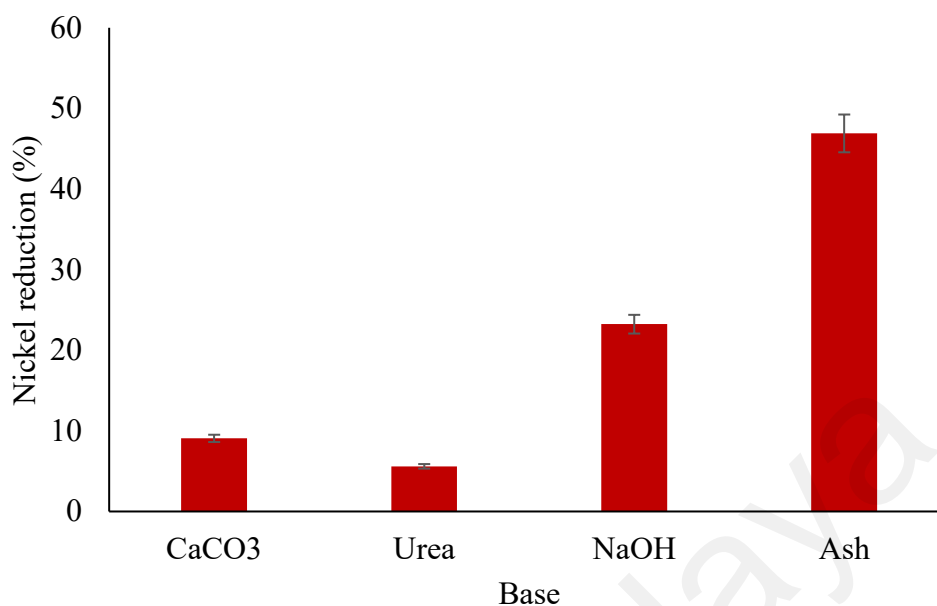


Figure 4.9. Effect of different basic pretreatment on nickel reduction.

4.4. Determination of contact time for ash-treated rice husk

Further study was performed to investigate the time needed for ash-treated rice husk to reach equilibrium in the nickel adsorption. The experimental parameters used were 100 ppm Ni at pH 6, stirring speed at 180 rpm and adsorbent dose of 4.0g/L. The treatment was prolonged for two hours to ensure maximum reduction had taken place. The data showed that nickel reduction became constant after about 15 min into treatment (Figure 4.10). The difference between adsorption time of untreated rice husk and ash-treated rice husk showed that pretreatment could have altered the structure of the rice husk by reducing recalcitrant materials and making functional groups available for binding. In comparison with the studies of Cu and Pb adsorption with TARH (Wong *et al.*, 2003), the rapid uptake of Ni using ash-treated rice husk was found to be faster, as it happened in about the first 40 mins into adsorption.

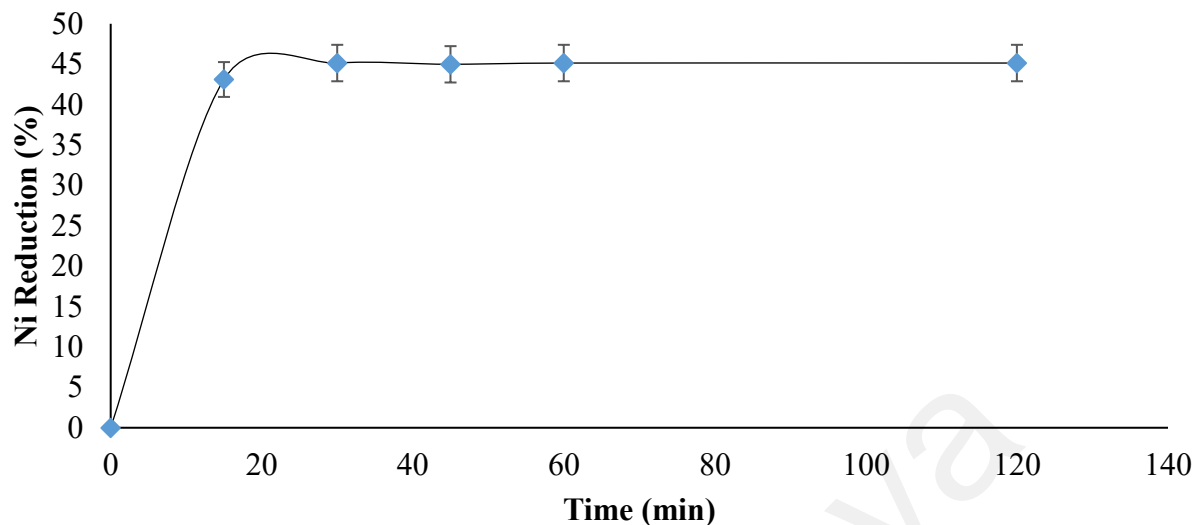


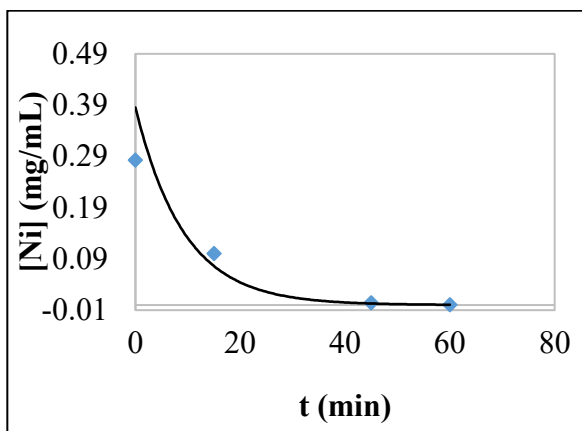
Figure 4.10. Contact time between ash-treated rice husk and nickel solution on the percent of nickel reduction after 2-hour treatment in industrial wastewater.

4.5. Kinetic study of nickel reduction using ash-treated rice husk

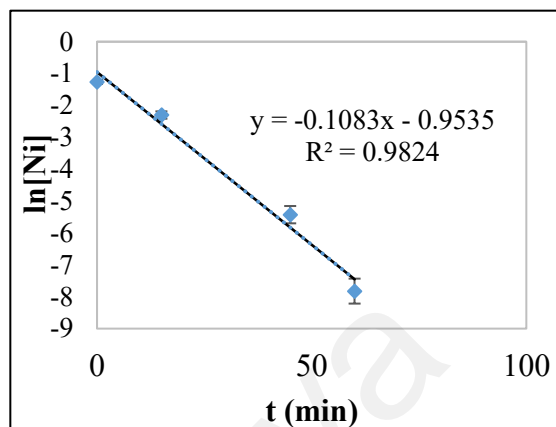
Kinetic analyses were performed based on the data collected from the batch system in favorable condition that was initial pH 6, at 23°C room temperature, agitation rate of 180 rpm, and adsorbent dose of 4.0 g/L. In order to determine the reaction order for the adsorption, the integrated rate laws were applied and the results are shown by Table 4.3 below. Based on the graphs in Figure 4.11, the plot $\ln[\text{Ni}]$ vs t gives a linear slope, $-k$ whereas the others are curved. Hence, the reaction was a first-order reaction.

Table 4.3 Integrated rate laws application to determine reaction order of nickel adsorption

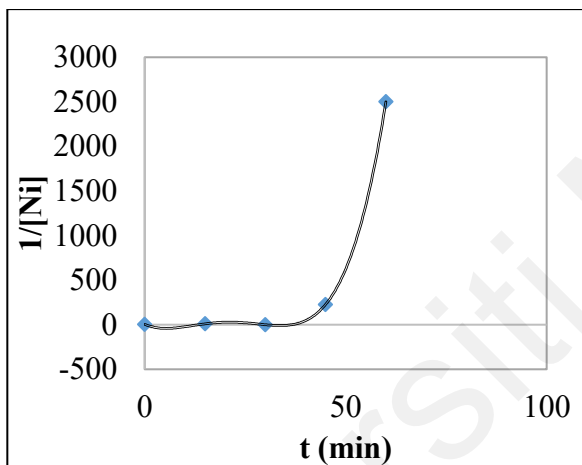
Reaction order	Kinetic plot	Slope	R^2
Zero	$[\text{Ni}]$ vs t	-	-
First	$\ln[\text{Ni}]$ vs t	$-k$	0.9824
Second	$\ln[\text{Ni}]$ vs t	-	-



(a)



(b)



(c)

Fig 4.11. Integrated rate law plots for Ni concentration versus time (t), (a) zero order reaction; (b) first order reaction; (c) second order reaction

4.6 Langmuir Adsorption Isotherm

This isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place (Dada *et al.*, 2012). Hence, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases (Vermeulan *et al.*, 1966). The isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. It assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based on these assumptions, Langmuir is represented by the following equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \dots \dots \dots \text{(Equation 2)}$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation (2) into linear form.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \dots \dots \dots \text{(Equation 3)}$$

Where:

C_e = the equilibrium concentration of adsorbate (mg/L-1)

q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)

q_m = maximum monolayer coverage capacity (mg/g)

K_L = Langmuir isotherm constant (L/mg).

The values of K_L were computed from the slope and intercept of the Langmuir plot of C_e/q_e versus C_e . The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant referred to as separation factor or equilibrium parameter (Webber & Chakravarti, 1974).

$$R_L = \frac{1}{1 + (K_L C_0)} \dots \dots \dots \text{(Equation 4)}$$

Where:

C_0 = initial concentration

K_L = the constant related to the energy of adsorption (Langmuir Constant)

According to Dada *et al.* (2012), R_L value indicates the adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$. From the data summarized in Table 4.4, the R_L is greater than 0 but less than 1 indicating that Langmuir isotherm is favourable. The maximum monolayer coverage capacity (q_m) from Langmuir Isotherm model was determined to be 0.237 mg/g, K_L (Langmuir isotherm constant) is 0.292 L/mg, R_L (the separation factor) is 0.482 indicating that the equilibrium sorption was favourable and the R^2 value is 0.9996 proving that the sorption data fitted well to the Langmuir Isotherm model.

Table 4.4 Langmuir Isotherm constants for the adsorption of Ni(II) ion unto rice husk

Metal ions	q_m (mg/g)	K_L (L/mg)	R_L	R^2
Ni(II)	0.237	0.292	0.482	0.9996

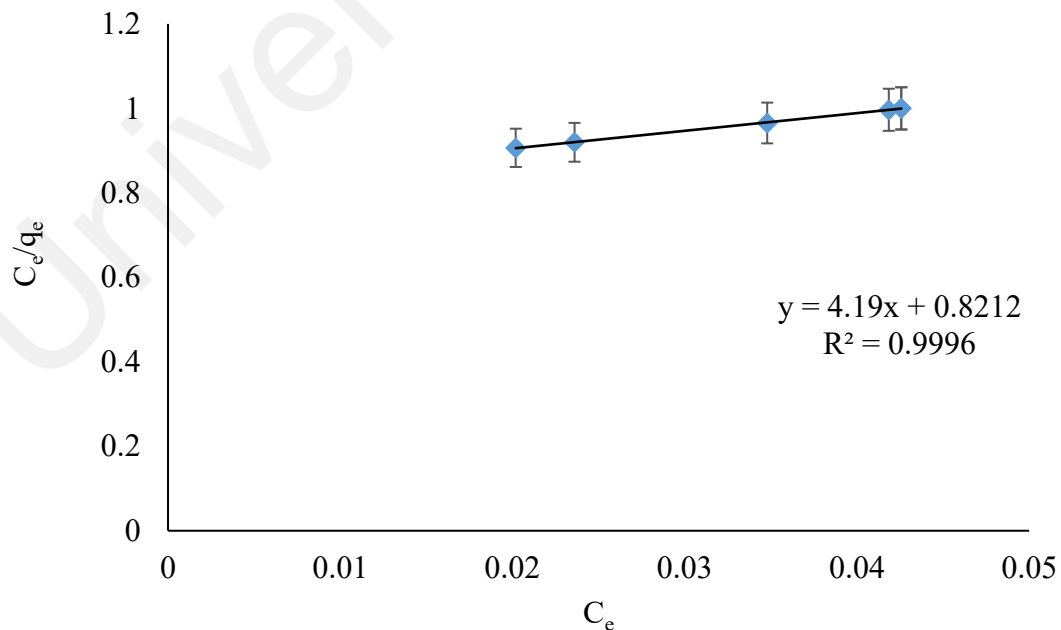


Figure 4.12. Langmuir Adsorption Isotherm

4.7. Effect of ash-treated rice husk on heavy metal adsorption in wastewater

From the results shown in Figure 4.9, rice husk that was pre-treated with ash shows the highest amount of nickel reduction during synthetic wastewater adsorption. Hence, ash-treated rice husk was used to study the adsorption process in industrial wastewater. Treatment was performed at optimal conditions based on the results collected from the optimization studies (pH 6, 180 rpm, 4.0 g/L adsorbent, 1 hr). Samples of untreated wastewater and treated were further analyzed for heavy metal ions concentration through ICP-OES and the results are shown in Table 4.5.

Table 4.5 Concentration of select heavy metal ions before and after treatment with ash-treated rice husk

Heavy metals	Initial concentration (ppm)	Final concentration (ppm)	% concentration removed
Cr	0.0025	0.0013	48.0
Cu	0.4477	0.2593	42.1
Ni	76.0748	70.3028	7.6
Zn	0.2456	0.2166	11.8

Based on Table 4.5, the ash-treated rice husk was found to reduce the concentration of the four heavy metals, with Cr showing the highest decrease in concentration. According to the Malaysia's Environmental Law, Environmental Quality (Industrial Effluents) Regulations (2009), the limit of nickel discharge is 0.2 ppm, which means that the wastewater from our studies has not been treated completely for it to be at a safe level. The reduction of

other heavy metals however, fell within safe standards. Zn reduction on the other hand needs another 0.01 ppm reduction for it to meet the parameter limit.

It was also notable that nickel reduction was not found to be feasible compared to the rest of the heavy metals as it only recorded 7.6% removal. This may be attributed to the highly concentrated sample of various heavy metals thus it would be recommended that a follow-up nickel assay be carried out using samples that have been serial diluted. A more extensive study of nickel biosorption using rice husk may also include the outcome of the surface of the pretreated rice husk that was used in the industrial wastewater sorption, which can be done by drying the husk and then analyzed by SEM. As for the nickel that was adsorbed on the husk, recovery of nickel may be conducted for future studies or it can be incinerated for disposal.

CHAPTER 5. CONCLUSIONS

SEM shows that the surface of rice husk has been exposed and becomes rough after pretreatment with base, which also means the unwanted lignin has been removed. FT-IR spectra and XRD both show there has been alteration in the structure of rice husk after pretreatment, possibly changing the functional groups. pH 6 gives the optimum reduction of nickel concentration in synthetic nickel solution when using rice husk as the adsorbent. Equilibrium is faster when using rice husk that has been pretreated. The study found that the most effective alkaline pretreatment to remove nickel is by using ash. From the study, adsorbent dose affects nickel reduction directly. As more adsorbent is added, more reduction is observed. Initial concentration of nickel in solution affects adsorption. Increased initial nickel concentration gives less reduction of nickel. Because a number of heavy metals are usually found in contaminated wastewater, the competitive interaction between them has to be weighed as well. Nickel adsorption using rice husk was found to favor the Langmuir isotherm which assumes monolayer adsorption process. Further work will go into determining other sorption isotherms such as Freundlich as well as studying the effect of nickel adsorption in wastewater. Besides that, future studies can be researched to find out a better pre-treatment for rice husk that can uptake various heavy metals at once. The tested hypothesis that Ni(II) ions uptake in synthetic solution using alkaline-treated rice husk will be higher than using raw rice husk because the structure of the adsorbent has been modified, allowing more binding sites for adsorption was also proven.

REFERENCES

- Agency for Toxic Substances and Disease Registry (2005). *Toxicological profile for nickel*.
- Ahalya, N., Ramachandra, T. V., & Kanamadi, R. D. (2003). Biosorption of Heavy Metals. *Research Journal of Chemistry and Environment*, 7, 71-79.
- Babarinde, A., Babalola, J. O., & Sanni, R. A. (2006). Biosorption of lead ions from aqueous solution by maize leaf. *International Journal of Physical Sciences*, 1(1), 23-26.
- Bailey, S. E., Olin, T. J., Bricka, R. M., & Adrian, D. D. (1999). A review of potentially low-cost sorbents for heavy metals. *Water Research*, 33, 2469-2479.
- Barth, A. (2007). Infrared spectroscopy of proteins. *Bioenergetics*, 1767(9), 1073-1101.
- Bhattacharya, A. K., Mandal, S. N., & Das, S. K. (2006). Adsorption of Zn(II) from aqueous solution by using different adsorbents. *Chemical Engineering Journal*, 123(1-2), 43-51.
- Bishnoi, N. R., Bajaj, M., Sharma, N., & Gupta, A. (2004). Adsorption of Cr(VI) on activated rice husk carbon and activated alumina. *Bioresource Technology*, 91(3), 305-307.
- Borba, C. E., Guirardello, R., Silva, E. A., Veit, M. T., & Tavares, C. R. G. (2006). Removal of nickel (II) ions from aqueous solution by biosorption in a fixed bed column: experimental and theoretical breakthrough curves. *Biochemical Engineering Journal*, 30, 184-191.
- Burwell, S. M. (2014). *Report on carcinogens* (13th ed.). Research Triangle Park, NC: NTP, National Toxicology Program.
- Dada, A. O., Olalekan, A., Olatunya, A., & Dada, D. O. (2012). Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ onto phosphoric acid modified rice husk. *Journal of Applied Chemistry*, 3, 38-45.
- Danial, W. H., Abdul Majid, Z., Mohd Muhid, M. N., Triwahyono, S., Bakar, M. B., & Ramli, Z. (2015). The reuse of wastepaper for the extraction of cellulose nanocrystals. *Carbohydrate Polymers*, 118, 165-169.
- Environmental Quality (Industrial Effluent) Regulations (2009).

- Fan, M., Dai, D., & Huang, B. (2012). Fourier Transform Infrared Spectroscopy for Natural Fibres. In S. Salih (Ed.), *Fourier Transform - Material Analysis* (45-68). InTech.
- Flores-Garnica, J. G., Morales-Barrera, L., Pineda-Camacho, G., & Cristiani-Urbina, E. (2013). Biosorption of Ni(II) from aqueous solutions by *Litchi chinensis* seeds. *Bioresource Technology*, 136(Supplement C), 635-643.
- Fourest, E., & Roux, J. C. (1992). Heavy metal biosorption by fungal mycelia by-product mechanisms and influence of pH. *Applied Microbiology and Biotechnology*, 37(13), 399-403.
- Gaballah, I., Goy, D., Allain, E., Kilbertus, G., & Thauront, J. (1997). Recovery of copper through decontamination of synthetic solutions using modified barks. *Metallurgical and Materials Transactions B*, 28(1), 13-23.
- Guo, Y., Qi, J., Yang, S., Yu, K., Wang, Z., & Xu, H. (2003). Adsorption of Cr(VI) on micro- and mesoporous rice husk-based active carbon. *Materials Chemistry and Physics*, 78(1), 132-137.
- Hanafiah, M. A. K. M., Ngah, W. S. W., Zakaria, H., & Ibrahim, S. C. (2007). Batch study of liquid-phase adsorption of lead ions using lalang (*Imperata cylindrica*) Leaf Powder. *Journal of Biological Sciences*, 7, 222-230.
- Hanafiah, M. A. K. M., Ngah, W. S. W., Ibrahim, S. C., H, Z., & Ilias, W. A. H. W. (2006). Kinetics and thermodynamic study of lead adsorption from aqueous solution onto rubber (*Hevea brasiliensis*) Leaf Powder. *Journal of Applied Science*, 6(13), 2762-2767.
- Ho, Y.-S., Chiu, W.-T., Hsu, C.-S., & Huang, C.-T. (2004). Sorption of lead ions from aqueous solution using tree fern as a sorbent. *Hydrometallurgy*, 73(1-2), 55-61.
- Johnson, P. D., Watson, M. A., Brown, J., & Jefcoat, I. A. (2002). Peanut hull pellets as a single use sorbent for the capture of Cu(II) from wastewater. *Waste Management*, 22(5), 471-480.
- Kadirvelu, K., Thamaraiselvi, K., & Namasivayam, C. (2001). Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresource Technology*, 76(1), 63-65.
- Karunasagar, D., Krishna, M. V., Rao, S. V., & Arunachalam, J. (2005). Removal and preconcentration of inorganic and methyl mercury from aqueous media using a sorbent prepared from the plant *Coriandrum sativum*. *Journal of Hazardous Materials*, 118(1-3), 133-139.

- King, P., Srinivas, P., Kumar, Y. P., & Prasad, V. S. R. K. (2006). Sorption of copper(II) ion from aqueous solution by *Tectona grandis* l.f. (teak leaves powder). *Journal of Hazardous Materials*, 136(3), 560-566.
- Kumar, P. S., Ramakrishnan, K., Kirupha, S. D., & Sivanesan, S. (2010). Thermodynamic and kinetic studies of cadmium adsorption from aqueous solution onto rice husk. *Brazilian Journal of Chemical Engineering*, 27, 347-355.
- Lee, C.-H., & Lee, C.-H. (2005). A study on nickel hydroxide crystallization characteristics. *Korean Journal of Chemical Engineering*, 22(5), 712-716.
- Malkoc, E., & Nuhoglu, Y. (2005). Investigations of nickel(II) removal from aqueous solutions using tea factory waste. *Journal of Hazardous Materials*, 127(1-3), 120-128.
- Naiya, T. K., Singha, B., & Das, S. K. (2011). FTIR study for the Cr (VI) removal from aqueous solution using rice waste. *International Proceedings of Chemical, Biological & Environmental Engineering*, 10, 114-119.
- Nakajima, A., & Sakaguchi, T. (1990). Recovery and removal of uranium by using plant wastes. *Biomass*, 21(1), 55-63.
- Nakbanpote, W., Thiravetyan, P., & Kalambaheti, C. (2002). Comparison of gold adsorption by *Chlorella vulgaris*, rice husk and activated carbon. *Minerals Engineering*, 15(7), 549-552.
- Nazir, M. S., Wahjoedi, B. A., Yussof, A. W., & Abdullah, M. A. (2013). Eco-friendly extraction and characterization of cellulose from oil palm empty fruit bunches. 8(2), 2161-2172.
- Nickel Institute (2017). About nickel: first and end uses of nickel. Retrieved from <http://nickelinstitute.org>
- Quek, S. Y., Wase, D. A. J., & Forster, C. F. (1998). The use of sago waste for the sorption of lead and copper. *Water SA*, 24.
- Rahman, I. A., & Ismail, J. (1993). Preparation and characterization of a spherical gel from a low-cost material. *Journal of Materials Chemistry*, 3, 931-934.
- Rahman, I. A., Ismail, J., & Osman, H. (1997). Effect of nitric acid digestion on organic materials and silica in rice husk. *Journal of Materials Chemistry*, 1505-1509.

- Rajalakshmi, R., Subhashini, S., & Lalitha, P. (2009). Usefulness of Activated Carbon Prepared from Industrial Wastes in the Removal of Nickel from Aqueous Solution. *E-Journal of Chemistry*, 6(2), 361-370.
- Rendle, D. F. (2003). X-ray diffraction in forensic science. *Rigaku Journal*, 19(2), 11-22.
- Saeed, A., Akhter, M. W., & Iqbal, M. (2005). Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. *Separation and Purification Technology*, 45(1), 25-31.
- Sawalha, M. F., Peralta-Videa, J. R., Romero-Gonzalez, J., & Gardea-Torresdey, J. L. (2006). Biosorption of Cd(II), Cr(III), and Cr(VI) by saltbush (*Atriplex canescens*) biomass: thermodynamic and isotherm studies. *Journal of Colloid and Interface Science*, 300(1), 100-104.
- Tarley, T. C. R., Costa Ferreira, S. L., & Zezzi Arruda, M. A. (2004). Use of modified rice husks as a natural solid adsorbent of trace metals: characterisation and development of an on-line preconcentration system for cadmium and lead determination by FAAS. *Microchemical Journal*, 77(2), 163-175.
- Villaescusa, I., Fiol, N., Martínez, M. a., Miralles, N., Poch, J., & Serarols, J. (2004). Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. *Water Research*, 38(4), 992-1002.
- Wan Ngah, W. S., & Hanafiah, M. A. K. M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. *Bioresource Technology*, 99, 3935-3948.
- Williams, C. J., Aderhold, D., & Edyvean, R. G. J. (1998). Comparison between biosorbents for the removal of metal ions from aqueous solutions. *Water Research*, 32(1), 216-224.
- Wong, K. K., K., L. C., Low, K. S., & Haron, M. J. (2003). Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. *Chemosphere*, 50(1), 23-28.