

# Adsorption of Ni(II) onto Chemically Modified Spent Grated Coconut (*Cocos Nucifera*)

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**Abstract.** A new adsorbent of plant waste origin from coconut processing food factory was explored for removing Ni(II) from aqueous solutions. Several parameters such as pH, dosage, concentration and contact time were studied to obtain optimum conditions for treatment of Ni(II) contaminated wastewater. Spent grated coconut (*Cocos nucifera*) treated with sulfuric acid (SSGC) showed good adsorption capacity for Ni(II) ion. The amount adsorbed was affected by solution pH with the highest value achieved at pH 5. Other optimum conditions found were; dosage of 0.02 g, and 60 min of equilibrium time. Ni(II) adsorption obeyed the pseudo-second order kinetic model which suggested that chemisorption mechanism occurred in the adsorption process. The equilibrium data presented a better fitting to the Langmuir isotherm model, an indication that monolayer adsorption occurred onto a homogeneous surface. The maximum adsorption capacity,  $q_{\max}$  was 97.09 mg g<sup>-1</sup>, thus SSGC can be classified as good and comparable with other plant waste adsorbents.

## 1. Introduction

Coconut tree (*Cocos nucifera*) is one of the members of Arecaceae (palm family) that grows especially in the tropics and is considered as one of the important crops in Malaysia. It is easily grown and can be found in different types of soil such as loamy, laterite, coastal sandy and reclaimed soils. Coconut is a versatile plant, having a multipurpose source of food and non-food products. In Malaysia, coconut waste is easily obtained due to its major consumption by local community. Spent grated coconut (SGC) from a defatted coconut residue is a by-product of a coconut milk factory. After the extraction of coconut milk, SGC fiber by-product finds other applications such as fertilizers and animal feed [1].

The term heavy metal is referring to any metallic element presence in periodic table which has a relatively high density, toxic and mutagenic effect at low concentration. The excessive release of heavy metal into the environment due to industrialization activities has become a major source of water pollution. The chemical exposure happens when sources such as factory, incinerator, tank, plant, landfill and chemical store released toxic level of chemicals to the surrounding and come in contact with human. Zinc, lead, cadmium, mercury, chromium and nickel are the known type of heavy metals which are commonly found in wastewater discharge. Due to their non-biodegradable and persistent in nature, heavy metals can accumulate in the soil and thus harm the ecosystem. Heavy metals enter human bodies via three pathways; ingestion, inhalation, and absorption through our large organ (skin) and mucous membrane and will be stored in human body tissues [2]. If exposed to human, heavy metals will be accumulated in body tissues, bound to proteins, impair enzymatic activity, slowly poison organ and ultimately result in fatality [3]. Ni(II) is one of the heavy metals of concern and the maximum permissible in aqueous solution is 0.02 mg L<sup>-1</sup> based on WHO guidelines [4].



In wastewater removal technique, adsorption is employed to remove heavy metal ions at low concentrations which is better than ion-exchange, electrolysis, chemical precipitation, membrane separation, carbon adsorption and co-precipitation which are used at higher concentrations. In this experiment, spent grated coconut was used as an adsorbent because it is quite cheap, low economic value and easy to obtain from local market. Most of the adsorption studies have been focused on plant waste such as corn silk [5], rape straw [6], sugarcane bagasse [7], lalang (*Imperata cylindrical*) leaf powder [8], sugarcane bagasse pith [4] and husk of *Lathyrus sativus* [9].

The aim of this work was to evaluate the adsorption potential of sulfuric acid treated coconut spent grated for Ni(II) removal from aqueous solutions. Experiments were done in a batch system to study the effect of initial pH, biosorbent dosage and initial Ni(II) ion concentration. The adsorption was modelled by kinetic models to understand the mechanism while the isotherm models were used to model the adsorption equilibrium.

## 2. Methodology

### 2.1. Chemical treatment of spent grated coconut (*Cocos nucifera*)

The sample of spent grated coconut was collected from a food factory in Kuching, Malaysia. The pre-treatment and modification methods were adapted from our recent study [1]. The spent grated coconut was dried in an oven at 105 °C overnight and designated as SGC. It was washed with hexane (R&M Chemicals, UK) in the ratio of 1.0 g SGC to 10 mL of hexane (1:10, w/v) and was stirred using magnetic stirrer for 16 h. This method removed fat and eliminated the organic interferences in sample matrix. The pre-treated sample was filtered and dried at 70 °C for 3 h. The hexane-washed SGC was labelled as HSGC. Acid treatment was then carried out to enhance the adsorption. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) in particular is widely used where it is able to improve pore development. The dehydrating effect of a concentrated  $\text{H}_2\text{SO}_4$  is known to reduce the carbon atoms in a plant. The modification involved mixing 30 g of HSGC with 500 mL (3.0 M)  $\text{H}_2\text{SO}_4$  (ratio of 3:50, w/v) at 100 °C. The mixture was stirred continuously at 480 rpm for 3 h, cooled to room temperature before washed twice with 1 L deionized water each time. The slurry was then filtered and soaked in 1 L (1.5% w/v)  $\text{NaHCO}_3$  solution for 24 h to remove excess acid. Next, the sample was washed thoroughly with distilled water until the pH of the effluent was close to 7. The samples were dried for overnight in an oven at 105 °C, ground and sieved to obtain average particle size of 120-250  $\mu\text{m}$ . The  $\text{H}_2\text{SO}_4$  modified powder was labelled as SSGC

### 2.2. Nickel batch adsorption experiment

All batch adsorption experiments were carried out in duplicates and the results were reported as average. All chemicals used were of analytical reagent grade. The standard solution of Ni(II) (1000  $\text{mg L}^{-1}$ ) was purchased from Fluka (Germany). Experimental solutions of the desired Ni(II) concentrations were obtained by successive dilutions from the standard Ni(II) solution. For adsorption experiments, a known weight of the adsorbent was mixed with 50 mL Ni(II) solutions in a conical flask at room temperature ( $30.0 \pm 0.5$  °C), shaken at 120 stroke/min for a certain period of time. The initial pH of Ni(II) solution was fixed at 5 by adding 1 M hydrochloric acid (HCl) or sodium hydroxide (NaOH) solutions.

The effect of pH was studied over a pH range of 2-5 to avoid precipitation of  $\text{Ni}(\text{OH})_2$ . To study the effect of dosage, the weight of adsorbent was varied from 0.01 to 0.10 g. The effects of Ni(II) concentration, contact time and kinetics were evaluated by shaking SSGC with Ni(II) solutions (5, 10 and 30  $\text{mg L}^{-1}$ ) at various time intervals (5-120 min). The isotherm study was conducted by equilibrating Ni(II) solutions (5-80  $\text{mg L}^{-1}$ ) with 0.02 g SSGC. After adsorption, the mixture was filtered and the filtrate was analysed for Ni(II) content using an Atomic Absorption Spectrometer (PinAAcle 900T, PerkinElmer, USA). The amount of Ni(II) adsorbed,  $q_e$ , ( $\text{mg g}^{-1}$ ) and percentage of removal were calculated by using equation (1) and equation (2) respectively:

$$q_e = \frac{C_o - C_e}{m} V \quad (1)$$

$$\text{Removal}(\%) = \frac{C_o - C_e}{C_o} \times 100\% \quad (2)$$

where,  $C_o$  ( $\text{mg L}^{-1}$ ) and  $C_e$  ( $\text{mg L}^{-1}$ ) are Ni(II) concentrations before and after adsorption, respectively;  $V$  (L) is the volume of Ni(II) solution, and  $m$  (g) is the weight of SSGC.

### 3. Results and discussion

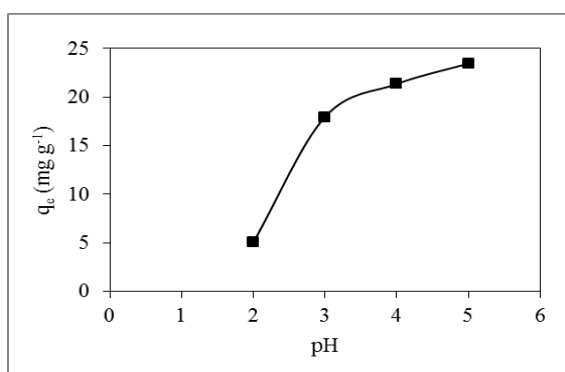
#### 3.1. Effect of pH

It is well recognized that the pH is an important parameter governing the adsorption of metal ions by sorbent and impacted the adsorption process. Figure 1 shows the change in pH contributed to the removal efficiency. Theoretically, the solution pH significantly affects the metal chemistry and the surface properties of adsorbent. The pH also affects the ionization states of functional groups, such as carboxyl and hydroxyl on cellulose-rich adsorbents.

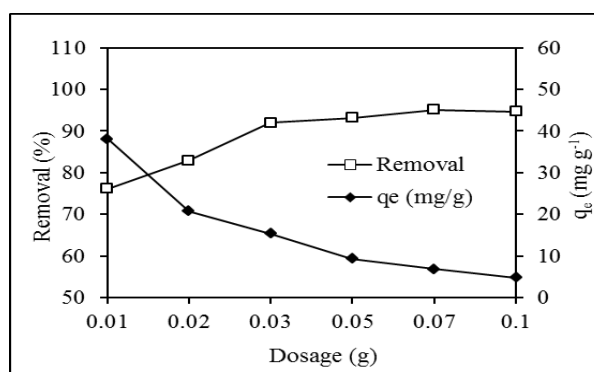
The optimum pH was 5 with highest amount of Ni(II) adsorbed ( $q_e$ ) of  $23.43 \text{ mg g}^{-1}$ . Less adsorption took place at the initial pH 2 (19.82%) that explained on the basis of active sites protonation, resulting in  $\text{H}^+$  and  $\text{Ni}^{2+}$  competition to occupy the active sites. A continuous increase in  $q_e$  occurred at the pH range of 2-5. The increase in the  $q_e$  was due to reduction of the electrostatic repulsion between the surface of SSGC and  $\text{Ni}^{2+}$  ion in bulk liquid.

#### 3.2. Effect of adsorbent dosage

From Figure 2,  $q_e$  decreased from  $38.08$  to  $4.73 \text{ mg g}^{-1}$  as dosage was increased from  $0.01$  to  $0.1 \text{ g}$ . The percentage removal of Ni(II) however increased from  $76.16$  to  $94.67\%$ . The  $q_e$  at low dosage was high because Ni(II) could easily access the adsorption sites. The  $q_e$  however decreases at higher amount of dosage which could be due to the aggregation of adsorbent particles resulting in a decrease in the effective sites for adsorption. Thus the optimum dosage was selected as  $0.02 \text{ g}$  of which it achieved the optimum percentage of removal and the amount of Ni(II) absorbed.



**Figure 1.** Effect of pH on Ni(II) adsorption onto SSGC ( $C_o$ :  $10 \text{ mg L}^{-1}$ ; dosage:  $0.02 \text{ mg}$ ).



**Figure 2.** Effect of adsorbent dosage on Ni(II) adsorption onto SSGC ( $C_o$ :  $10 \text{ mg L}^{-1}$ ; pH: 5).

#### 3.3. Effects of nickel concentration, contact time and adsorption kinetics

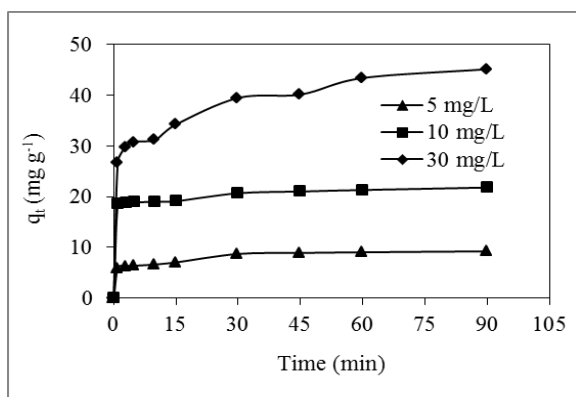
Figure 3 shows the adsorption data at different initial Ni(II) concentrations and contact time. It can be clearly seen that the  $q_e$  and equilibrium time are dependent on the concentration on Ni(II). The  $q_e$  increased with contact time for all Ni(II) concentrations. The percentage removal of Ni(II) ions was initially increased due to the high availability of surface area of SSGC. The amount adsorbed remain unchanged and reached equilibrium within 30 min for Ni(II) concentrations of both  $5 \text{ mg L}^{-1}$  and  $10 \text{ mg L}^{-1}$ , and extended up to 60 min for Ni(II) concentrations of  $30 \text{ mg L}^{-1}$ .

The pseudo-first order and pseudo-second order models were used to examine the kinetics adsorption process. The pseudo-first order indicates the intraparticle diffusion model which adsorption is controlled by diffusion into the boundary layer [10] while pseudo-second indicates the chemisorption process. The correlation coefficient ( $R^2$ ) can be evaluated and the adsorption capacities between calculated and experimental values can be compared. The expression of pseudo-first order [11] and pseudo-second order models [12] are given by equations (3) and (4) respectively:

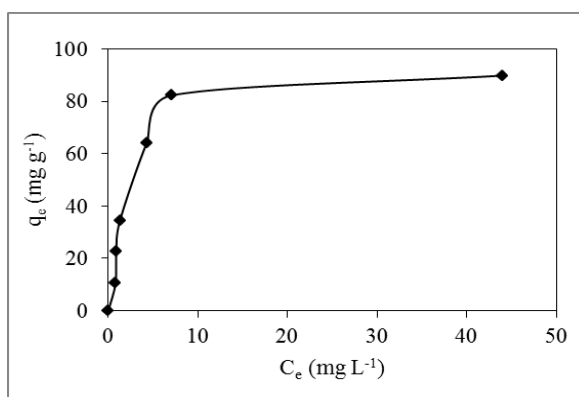
$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (4)$$

The symbol of  $q_e$  indicates the amount of Ni(II) adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium, while  $q_t$  indicates that amount of Ni(II) adsorbed at time  $t$  (min),  $k_1$  is the rate constant of adsorption process ( $\text{min}^{-1}$ ) of the pseudo-first order,  $k_2$  ( $\text{g/mg.min}$ ) is the pseudo-second order rate constant while  $h$  ( $\text{mg/g.min}$ ) is the initial adsorption rate and can be calculated by using the formula;  $h=k_2q_e^2$ .



**Figure 3.** Effects of initial concentration and contact time on Ni(II) adsorption onto SSGC (pH 5; dosage: 0.02 mg)..



**Figure 4.** Isotherm plot of Ni(II) adsorption by SSGC (pH 5; dosage: 0.02 mg)..

Table 1 shows the pseudo-first order and pseudo-second order parameters at different Ni(II) concentrations. From this table, the  $R^2$  values were between 0.867–0.969 while the rate constants ( $k_1$ ) were in the range of 0.010 to 0.017  $\text{min}^{-1}$  using pseudo-first order model. The low  $R^2$  values for all concentrations suggested that it is less appropriate to use pseudo-first order expression. However, the  $R^2$  values were much better for the pseudo-second order which were in the range of 0.954 to 0.999. From the calculations, the values of  $q_{e, \text{cal}}$  were close to the values of  $q_{e, \text{exp}}$ . Thus the Ni(II) adsorption follows the pseudo-second order kinetic model which suggested the chemisorption process.

**Table 1.** Pseudo-first order and pseudo-second order parameters at different concentrations of Ni(II).

Ni(II) ( $\text{mg L}^{-1}$ )	$q_{e, \text{exp}}$ ( $\text{mg g}^{-1}$ )	Pseudo-first order			Pseudo-second order			
		$q_{e, \text{cal}}$ ( $\text{mg g}^{-1}$ )	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_{e, \text{cal}}$ ( $\text{mg g}^{-1}$ )	$k_2$ ( $\text{g/mg.min}$ )	$h$ ( $\text{mg/g.min}$ )	$R^2$
5	9.230	2.735	0.016	0.867	9.372	0.050	4.400	0.998
10	21.820	2.805	0.017	0.969	21.787	0.049	23.148	0.999
30	45.167	1.858	0.010	0.944	45.249	0.008	16.949	0.954

### 3.4. Adsorption Isotherm

The isotherm explains the relationship between the amount of Ni(II) adsorbed ( $q_e$ ,  $\text{mg g}^{-1}$ ) and the concentration of adsorbate in bulk solution ( $C_e$ ,  $\text{mg L}^{-1}$ ) at a given temperature under equilibrium conditions. The term adsorption equilibrium is identified when the rate of adsorbate adsorbed is equal to the rate of adsorbate being desorbed from the adsorbent. The adsorption isotherm results are shown in Figure 4. The values of adsorption capacities increased as the concentration of Ni(II) increased. The highest  $q_e$  observed for the Ni(II) adsorption onto SSGC was  $89.91 \text{ mg g}^{-1}$ .

The adsorption isotherm data was further analysed by using the Langmuir and Freundlich isotherm models. The Langmuir isotherm model indicates that there is a limited area available for adsorption, the adsorbate is adsorbed as a monolayer molecule. The Freundlich model meanwhile, assumes that the adsorbent surface sites have different binding energies which indicate the multilayer adsorption behaviour of adsorbate molecules onto the heterogeneous surface of the adsorbent [13]. The linearized Langmuir and Freundlich isotherm expressions are represented in equations (5) and (6) respectively:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (5)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where  $q_e$  is the amount adsorbed at equilibrium,  $q_{\max}$  is the maximum adsorption capacity ( $\text{mg g}^{-1}$ ),  $b$  is a constant ( $\text{L mg}^{-1}$ ) related to the energy of adsorption which reflects the affinity between the adsorbent and the adsorbate,  $C_e$  is the equilibrium Ni(II) ion concentration ( $\text{mg L}^{-1}$ ).  $K_F$  and  $n$  are the maximum adsorption capacity ( $\text{mg g}^{-1}$ ) and adsorption intensity of the adsorbate ions on the adsorbent, respectively.

Table 2 presents the calculated parameters obtained from the linearized plots (not shown) of Langmuir and Freundlich models. The results revealed that the experimental equilibrium data had been in good agreement with Langmuir model. Based on  $R^2$  value and the close values of  $q_{e, \text{exp}}$  and  $q_{e, \text{cal}}$ , Langmuir model was favourable and suited the adsorption of Ni(II) onto SSGC. The high  $R^2$  values indicated that the model was suitable for describing the tested system under the concentration range studied, suggesting that Ni(II) adsorption was limited to monolayer coverage. This indicates that the surface is relatively homogeneous in terms of functional group where interaction occurred. However, the Freundlich coefficient of correlation value obtained for the Ni(II) adsorption on SSGC was lower (0.728) although the  $n$  value obtained was 2.17. The  $n$  value over 1 indicated the favourable adsorption [9]. These conclude that the adsorption data fitted the Langmuir model with  $q_{\max}$  recorded as  $97.09 \text{ mg g}^{-1}$  better than the Freundlich model.

**Table 2.** Langmuir and Freundlich isotherm constants and correlation coefficients.

$q_{e, \text{exp}}$ ( $\text{mg g}^{-1}$ )	Langmuir			Freundlich		
	$q_{\max}$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_F$ ( $\text{mg g}^{-1}$ )	$n$	$R^2$
89.91	97.09	0.32	0.988	28.59	2.17	0.728

Adsorption capacities of other adsorbents for the removal of Ni(II) are given in Table 3 for comparison and showed that SSGC is an effective adsorbent for the removal of Ni(II) from aqueous solutions.

**Table 3.** Comparison of adsorption capacities by various adsorbents.

Adsorbent	Solution pH	C <sub>o</sub> (mg L <sup>-1</sup> )	q <sub>max</sub> (mg g <sup>-1</sup> )	Reference
Sugarcane bagasse (untreated)	5	10-200	2.23	[7]
NaOH treated <i>Imperata cylindrica</i>	5	5-50	6.96	[8]
Husk of <i>Lathyrus sativus</i>	5	10-1000	15.70	[9]
Sugarcane bagasse pith (untreated)	6.5	50-1000	73.56	[4]
SSGC	5	5-80	97.09	This study
Sugarcane bagasse pith (activated carbon)	6.5	50-1000	140.85	[4]

#### 4. Conclusions

This study revealed that the optimum pH was reached at pH 5.0 and the adsorbent dosage of 0.02 g. The initial adsorption rate was fast and reached equilibrium in less than 60 min. The adsorption kinetics followed the pseudo-second order kinetic model which suggested the chemisorption process. It has been found that one gram of the SSGC could adsorb 97.09 mg Ni(II) and the adsorption process was best fitted to Langmuir isotherm. Thus, this work showed that SSGC is a potential adsorbent for the removal of Ni(II) from aqueous solutions.

#### Acknowledgment

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