PAPER • OPEN ACCESS

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

To cite this article: F I Hamzah et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 205 012009

View the article online for updates and enhancements.

You may also like

- Identification of morphological characters and kinship of coconut genotypes (*Cocos nucifera* L.) in Aceh Tamiang District, Aceh H Setiado, M A Sinaga, D S Hanafiah et al.
- Inhibitory power of young coconut fiber ethanol extract (Cocos nucifera Linn) on the growth of Bacteria staphylococcus aureus and Escherichia coli in tofu N K Sumarni, Rahmawati and Ruslan
- Preparation and characterization of alkali treated cocos nucifera var aurantiaca peduncle fibers reinforced epoxy composites
 K J Nagarajan, A N Balaji, N R Ramanujam et al.





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 3.145.15.1 on 07/05/2024 at 20:43

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

F I Hamzah¹, K Khalid² and M A K M Hanafiah²

¹ Faculty of Bioresource and Food Industry, Universiti Sultan Zainal Abidin 22000 Besut, Terengganu, Malaysia, ² Faculty of Applied Sciences, Universiti Teknologi MARA, Cawangan Pahang,

26400 Bandar Tun Razak Jengka, Pahang, Malaysia

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⁻¹, thus SSGC can be classified as good and comparable with other plant waste adsorbents.

1. Introduction

Coconut tree (Cocus 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^{-1} based on WHO guidelines [4].

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd 1

The 2nd International Conference on Materials Engineering and NanotechnologyIOP PublishingIOP Conf. Series: Materials Science and Engineering 205 (2017) 012009doi:10.1088/1757-899X/205/1/012009

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 pretreatment 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 (H_2SO_4) in particular is widely used where it is able to improve pore development. The dehydrating effect of a concentrated H₂SO₄ is known to reduce the carbon atoms in a plant. The modification involved mixing 30 g of HSGC with 500 mL (3.0 M) H_2SO_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)NaHCO₃ 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 µm. The H₂SO₄ 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 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 $(30.0\pm0.5)^{\circ}$ 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 Ni(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 mg L^{-1}) at various time intervals (5-120 min). The isotherm study was conducted by equilibrating Ni(II) solutions (5-80 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, (mg g⁻¹) and percentage of removal were calculated by using equation (1) and equation (2) respectively:

The 2nd International Conference on Materials Engineering and NanotechnologyIOP PublishingIOP Conf. Series: Materials Science and Engineering 205 (2017) 012009doi:10.1088/1757-899X/205/1/012009

$$q_e = \frac{C_o - C_e}{m} V \tag{1}$$

$$\operatorname{Removal}(\%) = \frac{C_{o} - C_{e}}{C_{o}} \times 100\%$$
⁽²⁾

where, $C_o (mg L^{-1})$ and $C_e (mg L^{-1})$ 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 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 H⁺ and Ni²⁺ 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 Ni²⁺ ion in bulk liquid.

3.2. Effect of adsorbent dosage

From Figure 2, q_e decreased from 38.08 to 4.73 mg g⁻¹ as dosage was increased from 0.01 to 0.1 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 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_0 : 10 mg L⁻¹; dosage: 0.02 mg).

Figure 2. Effect of adsorbent dosage on Ni(II) adsorption onto SSGC (C_0 : 10 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 mg L⁻¹ and 10 mg L⁻¹, and extended up to 60 min for Ni(II) concentrations of 30 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:

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

$$\frac{\mathbf{t}}{\mathbf{q}_{t}} = \frac{1}{\mathbf{h}} + \frac{1}{\mathbf{q}_{e}} \mathbf{t} \tag{4}$$

The symbol of q_e indicates the amount of Ni(II) adsorbed (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 (min⁻¹) of the pseudo-first order, k_2 (g/mg.min) is the pseudo-second order rate constant while h (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 R² values were between 0.867–0.969 while the rate constants (k₁) were in the range of 0.010 to 0.017 min⁻¹ using pseudo-first order model. The low R² values for all concentrations suggested that it is less appropriate to use pseudo-first order expression. However, the R² 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, cal} were close to the values of q_{e, 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).

		Pseu	udo-first or	der	Pseudo-second order			
Ni(II)	q _{e, exp}	q _{e, cal}	k1		q _{e,cal}	\mathbf{k}_2	h	
$(mg L^{-1})$	$(mg g^{-1})$	$(mg g^{-1})$	(\min^{-1})	\mathbf{R}^2	$(mg g^{-1})$	(g/mg.min)	(mg/g.min)	\mathbf{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

The 2nd International Conference on Materials Engineering and NanotechnologyIOP PublishingIOP Conf. Series: Materials Science and Engineering 205 (2017) 012009doi:10.1088/1757-899X/205/1/012009

3.4. Adsorption Isotherm

The isotherm explains the relationship between the amount of Ni(II) adsorbed (q_e , mg g⁻¹) and the concentration of adsorbate in bulk solution (C_e , 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 mg g⁻¹.

The adsorption isotherm data was further analysed by using the Langmuir and Freudlich 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:

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

$$\log q_{\rm e} = \log K_{\rm F} + \frac{1}{n} \log C_{\rm e} \tag{6}$$

where q_e is the amount adsorbed at equilibrium, q_{max} is the maximum adsorption capacity (mg g⁻¹), b is a constant (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 (mg L⁻¹). K_F and n are the maximum adsorption capacity (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 R² value and the close values of $q_{e, exp}$ and $q_{e, cal}$. Langmuir model was favourable and suited the adsorption of Ni(II) onto SGCC. The high R² 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 occured. 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 mg g⁻¹ better than the Freundlich model.

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

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

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.

The 2nd International Conference on Materials Engineering and Nanotechnology IOP Conf. Series: Materials Science and Engineering 205 (2017) 012009 doi:10.1088/1757-899X/205/1/012009

Solution C_{o} q_{max} Adsorbent Reference $(\underline{mg} L^{-1})$ $(mg g^{-1})$ pН Sugarcane bagasse (untreated) 5 10-200 2.23 [7] NaOH treated Imperata cylindrica 5 5-50 6.96 [8] 5 [9] Husk of Lathyrus sativus 10-1000 15.70 Sugarcane bagasse pith (untreated) 6.5 50-1000 73.56 [4] SSGC 5 97.09 This study 5-80

6.5

50-1000

140.85

Table 3. Comparison of adsorption capacities by various adsorbents.

IOP Publishing

[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

This work was supported by UiTM Research Grant Scheme (Dana: 600-RMI/ST/DANA 5/5/Dst (179/2011)

References

- [1] Khalid K and Hanafiah M A K M 2014 Adv Mater Res. 970 192–7.
- [2] Song Q and Li J. 2015 Environ. Pollut. 196 450–61.

Sugarcane bagasse pith (activated carbon)

- [3] Demirbas A 2008 J. Hazard. Mater. 157(2-3) 220-9.
- [4] Anoop K K, Sreejalekshmi K G and Baiju R S 2011 Bioresour Technol. 102(22) 10239–47.
- [5] Yu H, Pang J, Ai T and Liu L 2016 J. Taiwan Inst. Chem. Eng. 62 21–30.
- [6] Wu Y and Wang L 2016 Procedia Environ. Sci 31 75–80.
- [7] Alom á I, Mart n-Lara M A, Rodr guez I L, Bl ázquez G and Calero M. 2012. J. Taiwan Inst. Chem. *Eng.* **43(2)** 275–81.
- [8] Hanafiah M A K M, Zakaria H and Wan N W S 2010 Clean Soil, Air, Water 38(3) 248-56.
- [9] Panda G C, Das S K, Bandopadhyay T S and Guha A K 2007 Colloids Surf B Biointerfaces 57(2) 135-42.
- [10] Piccin J S, Gomes C S, Feris L A and Gutterres M. 2012 Chem Eng J. 183 30-8.
- [11] Ho Y S and Mckay G 1998 Process Saf. Environ. Prot. 76 332-40.
- [12] Ho Y S, Ng J C Y and McKay G 2000 Sep. Purif. Rev. 29(2) 189–232.
- [13] Srivastava S, Agrawal S B and Mondal M K 2015 Ecol. Eng. 85 56-66.