ELSEVIER

Chemical Engineering Journal 137 (2008) 181–188

Chemical Engineering Journal

www.elsevier.com/locate/cej

Comparison of nickel adsorption from electroplating rinse water by coir pith and modified coir pith

A. Ewecharoen [a], P. Thiravetyan [a,*], W. Nakbanpote [b]

[a] *Division of Biotechnology, School of Bioresources and Technology, King Mongkut's University of Technology Thonburi, 83 Moo 8 Thakham, Bangkhuntien, Bangkok 10150, Thailand*

[b] *Pilot Plant Development and Training Institute, King Mongkut's University of Technology Thonburi, 83 Moo 8 Thakham, Bangkhuntien, Bangkok 10150, Thailand*

Received 19 October 2006; received in revised form 27 March 2007; accepted 1 April 2007

Abstract

The coir pith was used as an adsorbent for nickel removal because the coir pith contains high lignin (36%) and cellulose (44%). The optimum condition for nickel removal by coir pith in a batch system was solution pH 4–7, adsorbent dosage of 5% (w/v), an equilibrium contact time of 10 min and a temperature of 30 °C. The nickel adsorption was fitted to the Langmuir and Freundlich isotherms that showed that the maximum value of nickel adsorption ($q_{\max}$) by coir pith and modified coir pith were 9.5 and 38.9 mg g^{-1}, respectively. Sodium hydroxide increased metal binding site (free O$^-$) of modified coir pith. The mechanism of nickel adsorption by the coconut coir pith was confirmed by elution with sulfuric acid, which implied that it was chemisorption. The evidence showed that lignin and holo-cellulose are the main components in coir pith that played a major role in nickel adsorption. The main functional groups in coir pith that were involved in nickel adsorption were hydroxyl and methoxy groups. It was confirmed by X-ray adsorption spectroscopy (XAS) that the oxidation species of nickel involved in nickel adsorption by coir pith and modified coir pith was Ni(II).

Keywords: Coir pith; Nickel; Electroplating; Mechanism

1. Introduction

The level of heavy metal in environmental water has increased as a result of many factories such as electroplating, electronic equipment and battery storage. Electroplating involves the deposition of a thin protective layer (usually metallic) onto a prepared metal surface, using electrochemical processes. Any or all of the substances used in electroplating (such as acidic solutions, toxic metals and solvents) can be found in this wastewater. The heavy metals in waste waters included cadmium, chrome, lead, copper, zinc and nickel. The high level of Ni(II) causes to respiratory damage leading to cancer. Therefore, it is necessary to treat wastewater before it is discharged into natural water. The methods currently employed for the removal of nickel from wastewater are cation-exchange and precipitation [1–3]. However, these methods have several disadvantages that include high cost and toxic sludge. For this reason, these studies look for a low cost material that acts as an adsorbent to remove nickel in wastewater. Recently, biomaterials (fungal, yeast, bacteria and algae) or waste from industry and agriculture have been shown to be promising in this regard. The waste from industry and agriculture were used as adsorbents because these wastes are dead cells in which adsorption is easily controlled. The industrial wastes used in heavy metal adsorption were shrimp chitin [4], clay [5] and crab shells [6]. The agricultural wastes used in heavy metal adsorption were grape stalks [7], activated carbon from coir pith [8], activated carbon from apricot [9], rice bran [10], *Azadirachta indica* (Neem) leaf powder [11] and maple sawdust [12]. Data show that agricultural waste was interesting.

Thailand is an agricultural country that produces agricultural products (rice, coconut, pineapple). By products of coconuts such as coconut husks and coconut coir pith are a large problem and are sold at low costs. Hence, this by-product should be used for an increased value application. Coir pith is a waste from the coir industry. This is a major industry, where coconut is produced on a large scale. During the process of separating fiber from the

---

[*] Corresponding author. Tel.: +66 2 470 7535; fax: +66 2 452 3455.
E-mail address: paitip.thi@kmutt.ac.th (P. Thiravetyan).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.04.007

Nomenclature

C_e	equilibrium concentration (mg l^{-1})
C_o	initial concentration (mg l^{-1})
g	the relative centrifugal force
k_a	Langmuir constants
k_F	Freundlich constants
q_e	equilibrium adsorption capacity (mg g^{-1})
q_{max}	maximum adsorption capacity (mg g^{-1})
S.D.	standard deviation
v	volume (l)
w	weight (g)

Units

cm	centimeter
g	gram
l	liter
mg	milligram
mmol	milli-mole
M	molar (mole per liter)
N	normal
rpm	rate per minute
μm	micrometer
°C	degree of Celsius
%	percentage

coconut husk, a large volume of pith is collected. The coir pith contains large amounts of lignin and cellulose. Therefore, it can be used as an adsorbent to recover nickel. It not only reduces the cost of wastewater management but also adds value to waste.

The previous literature only showed that the coir pith could adsorb cadmium [13] and dye [14] but did not investigate the adsorption mechanism. Therefore, this research investigated the mechanism of nickel adsorption, adsorption capacity and adsorption isotherm of coir pith and modified coir pith. Modified coir pith was developed to enhance the adsorption capacity of coir pith. The effects of parameters such as pH, adsorbent dosage and contact time were also determined.

2. Materials

2.1. Coir pith preparation

Coir pith was obtained from a mattress factory in Prachuapkhirikhan province, Thailand. It was air dried at room temperature. Then it was ground and sieved by USA. Standard Sieve (Endecotts Ltd., USA) of 80, 120 and 200 mesh sizes, which are 180, 125 and 75 μm, respectively, with sieve shaker (Retsch RS200, Germany).

2.2. Modified coir pith was treated with NaOH

The modification of coir pith with 0.1N NaOH was as follows. Coir pith was mixed with 0.1N NaOH (1:10) for 2 h. After treatment with 0.1N NaOH, the excess NaOH from modified coir pith was washed with distilled water until the pH was constant at 7.4; and then the coir pith was dried in the air.

2.3. Real rinse water from electroplating wastewater

The nickel rinse water was collected from an electroplating factory, located in Samuthprakarn province (Thailand), with a Ni(II) concentration of 145 mg l^{-1}.

3. Methods

3.1. The effect of conditions (pH, contact time, temperature, adsorbent dosage and particle size)

3.1.1. Effect of pH

The effect of system pH was studied by varying the initial pH (2–7) of nickel rinse water by adjusting the pH with 1 M NaOH or 1 M H_2SO_4. After shaking the flask for a specified equilibrium time, the reaction mixtures were separated by a centrifuge (Heraeus Labofuge 200, UK) at the relative centrifugal force (RCF) of $2185 \times g$ for 10 min. Then, the residual Ni(II) in the supernatant was measured by inductively coupled plasma (ICP) spectroscopy (JY124, France). In addition, the pH of the system containing nickel rinse water and coir pith was also analyzed by a pH meter (Mettler delta340, USA).

The percent of nickel adsorption was determined by the following equation:

$$\text{Ni(II) adsorption}\,(\%) = \left[\frac{C_o - C_e}{C_o}\right] \times 100 \qquad (1)$$

where C_o and C_e are the initial and equilibrium concentration (mg l^{-1}), respectively.

3.1.2. Effect of contact time

The experiments were carried out by using 10 ml of nickel rinse wastewater (Ni(II) $\approx$ 145 mg l^{-1}) and a coir pith dosage of 5% (w/v) in a 15 ml bottle and then shaking the mixtures at 150 rpm for varying times (1–24 h) at 30 °C. After shaking, the samples were separated by centrifugation at $2185 \times g$ for 10 min. Then, the residual nickel concentration in the supernatant and pH of adsorption system was measured by ICP and a pH meter, respectively.

3.1.3. Effect of adsorbent dosage

The experiments were carried out using 10 ml of nickel rinse wastewater (Ni(II) $\approx$ 145 mg l^{-1}) and varying coir pith dosage from 1 to 10% (w/v) in a 15 ml bottle and then shaking the mixtures at 150 rpm at a specified equilibrium time and temperature. After shaking, the samples were separated by centrifugation at $2185 \times g$ for 10 min. The residual nickel concentration in the supernatant and pH of adsorption system was measured by ICP and a pH meter, respectively.

3.1.4. Effect of particle size of adsorbent

The particle size of adsorbent was sieving by sieve (US Standard sieve). The effect of particle size of adsorbent was studied by using 10 ml of nickel rinse wastewater (Ni(II) $\approx$ 145 mg l^{-1})

and varying sizes of coir pith of 5% (w/v) in a 15 ml bottle and then shaking the mixtures at 150 rpm for a specified equilibrium time and temperature. After shaking, the samples were separated by centrifugation at 2185 × *g* for 10 min. The residual nickel concentration in the supernatant and pH of adsorption system was measured by ICP and a pH meter, respectively.

3.2. Adsorption isotherm

The adsorption isotherm experiments were carried out by using 10 ml of nickel rinse wastewater (Ni(II) $\approx$ 145–1250 mg l^{-1}) and coir pith of 5% (w/v) in a 15 ml bottle then shaking the mixtures at 150 rpm for 2 h at 30 °C. After shaking, the samples were separated by centrifugation at 2185 × *g* for 10 min. The residual nickel concentration in the supernatant and pH of adsorption system was measured by ICP and a pH meter, respectively.

The adsorption capacity (q_e) was determined by the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

where C_o and C_e are the nickel concentration initial and equilibrium concentration (mg l^{-1}), respectively, V the volume of solution (l) and m is the mass of adsorbent (g).

3.2.1. Langmuir isotherm

The Langmuir isotherm was adopted for the estimation of maximum metal uptake. The Langmuir isotherm assumes monolayer adsorption and is given by the following equation:

$$\left(\frac{C_e}{q_e}\right) = \left(\frac{1}{k_a q_{\max}}\right) + \left(\frac{1}{q_{\max}}\right) C_e \tag{3}$$

where k_a and $q_{\max}$ are the Langmuir constants, indicative of maximum adsorption capacity, q_e the metal uptake (mg nickel g^{-1} of adsorbent) and C_e is the nickel concentration at equilibrium (mg l^{-1}).

3.2.2. Freundlich isotherm

The Freundlich isotherm can be applied to non-ideal sorption on multilayer sorption and is expressed by the following equation:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{4}$$

where k_F and $1/n$ are the Freundlich constants, q_e the metal uptake (mg nickel g^{-1} of adsorbent) and C_e is the nickel concentration at equilibrium (mg l^{-1}).

3.3. Elution

The experiment was studied in a column system; the Ni-adsorbed coir pith was made in a batch experiment, air dried and placed in the syringe. The Ni-adsorbed coir pith was eluted by sulfuric acid (0.0125 M H_2SO_4 and 0.025 M H_2SO_4, respectively). Before elution by sulfuric acid, the Ni-adsorbed coir pith was eluted using 5 ml of distilled water (three cycles). Elution was carried out (each of elution had three cycles) with 5 ml 0.0125 M H_2SO_4 and 10 ml 0.025 M H_2SO_4, respectively. Fractions were collected. The residual nickel concentration in the supernatant and pH of adsorption system was measured by ICP and a pH meter, respectively.

3.4. Mechanism of adsorption by the composition of coir pith

The coir pith components (lignin and holo-cellulose were extracted from coir pith by TAPPI method) have been investigated to determine their role in effective nickel adsorption. According to 5% (w/v) of the coir pith composed of 1.8% lignin and 2.2% holo-cellulose. The experiments were carried out using 10 ml of nickel rinse wastewater (Ni(II) $\approx$ 145 mg l^{-1}) and 1.8% lignin or 2.2% holo-cellulose in a 15 ml bottle and the mixtures were shaken at 150 rpm for 2 h at 30 °C. After shaking, the samples were separated by centrifugation at 2185 × *g* for 10 min. The residual nickel concentration in the supernatant and pH of adsorption system was measured by ICP and a pH meter, respectively.

3.5. Functional groups of the adsorbents

The functional groups on the surface of the adsorbents before and after adsorption were analyzed by a Fourier transform infrared spectrophotometer. The spectra of the adsorbent were acquired using the KBr disc technique. The samples were ground and well mixed with KBr in a ratio of 2 mg sample to 100 mg KBr and then compressed in the disc.

3.6. Determination of the oxidation number of nickel by X-ray adsorption spectroscopy (XAS)

Experiments were conducted at room temperature on the beam line (BL8) of the National Synchrotron Research Center (Thailand) with a double crystal Ge(220) for the XANES monochromator. X-ray absorption (XAS) spectra at the Ni K edge (8.333 keV) were obtained in transmission mode with two low-pressure air-filled ionization chambers. The saturated adsorbents were collected in a sample holder.

Reference materials used for X-ray absorption near-edge spectroscopy (XANES) measurements included Ni foil, Nickel from rinse water of electroplating, $NiSO_4{\cdot}6H_2O$ and $NiCl_2{\cdot}6H_2O$. The data from XANES were analyzed by a supporting program.

4. Results and discussion

4.1. The characteristics of the coir pith

The coir pith contained high lignin (36%) and cellulose (44%) as shown in Table 1. The IR spectrum shows the functional groups of coir pith (Fig. 1). The functional groups were methoxy and hydroxyl groups (lignin and cellulose which comprised coir pith). These functional groups in coir pith are involved in nickel adsorption.

Table 1
The characteristic, composition and particle size of coir pith

Characteristic		Composition		Particle size	
Constituents	Percentage	Constituents	Percentage	Size (μm)	Percentage by weight
Ash	9.6	Lignin	36.0	>180	5.52
Solubility in hot water	3.7	Holo-cellulose	43.8	125–180	6.27
Solubility in alcohol	2.8	α-Cellulose	27.8	75–125	13.05
Solubility in $Na_2(SO_4)$	50.7	β-Cellulose	2.1	<75	75.16
		γ-Cellulose	13.9		
		Pentosan	16.2		
		Etc	4.0		

4.2. *The effect of nickel adsorption*

The solution pH affected to nickel solubility and nickel precipitation. Therefore, the concentration of nickel in the electroplating rinse water (145 mg l^{-1}) was studied under initial pH range of 2–7. Fig. 2 shows that the concentration of nickel decreased at pH higher than 7.7. At higher pHs, hydroxide ions (OH^- ions) in the solution, that can bind with Ni(II) ions to hydroxide complexes form as the nickel hydroxide. Therefore, the system pH (coir pith with nickel solution) should not exceed 7.7.

The efficiency of nickel adsorption at initial pH of 2–3 was lower than another pH that had been used (Fig. 3). At low pH, the solution has a higher hydrogen ion (H^+ ions) concentration that competes with the adsorption of nickel ions by the adsorbent. It caused a decrease in the efficiency of nickel adsorption.

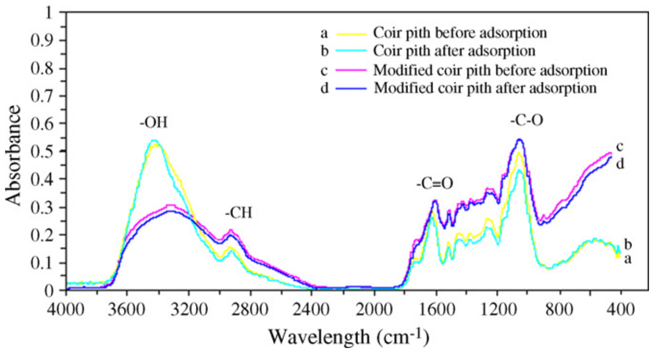

Fig. 1. IR spectra of coir pith and modified coir pith before and after nickel adsorption from electroplating rinse water.

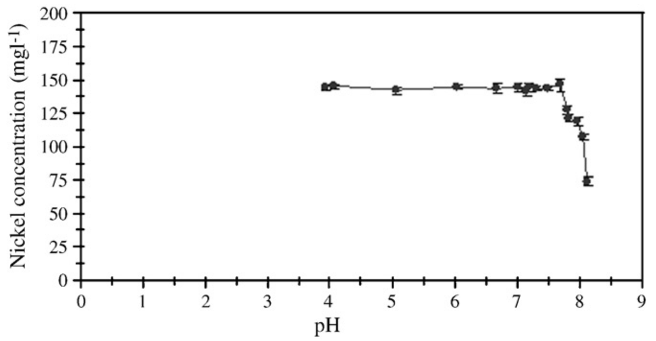

Fig. 2. Effect of pH on nickel solubility in electroplating rinse water (Ni(II) concentration of 145 mg l^{-1}, initial solution pH 3.92).

Fig. 4 shows how the adsorption of Ni(II) increased with increasing time. The adsorption of nickel was rapid and the maximum Ni(II) adsorption was reached at an equilibrium contact time at 10 min. At equilibrium contact time, the percent of Ni(II) adsorbed by coir pith was 88% at 5% (w/v) adsorbent dosage.

The effect of coir pith dosage was shown in Fig. 5. The percent of nickel adsorption increased with increasing dosages of coir pith and equilibrium dosages of coir pith were about 5% (w/v). However, data of the effect of coir pith dosage subjected to analysis of variance and means separation using the Duncan multiple range test (DMRT) by the same letter were not significantly different at $P \leq 0.05$, indicating that the effect of coir pith dosage by this process was not different at dosage of coir pith higher than 5% (w/v). The dosage $\geq$5% can not increase nickel removal. The reason behide that needed to be further studied.

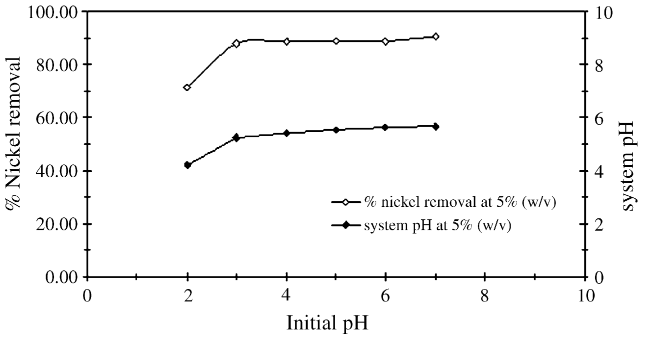

Fig. 3. Effect of initial solution pH on nickel removal from electroplating rinse water by coir pith (Ni(II) concentration of 145 mg l^{-1}).

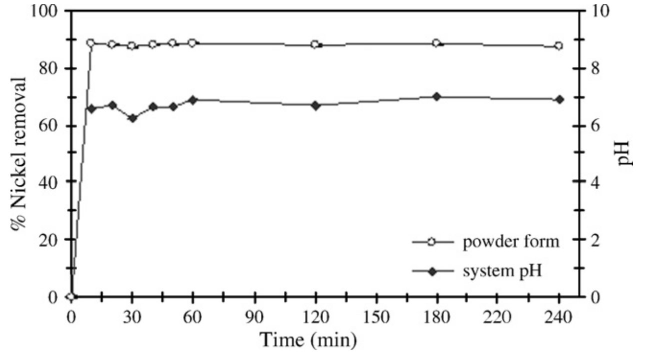

Fig. 4. Contact time on nickel removal from electroplating rinse water by coir pith (initial Ni(II) concentration of 145 mg l^{-1}, initial solution pH 3.92).

Table 2
Effect of particle size of coir pith on nickel removal from electroplating rinse water

Dosage (%)	Nickel removal (%)				
	Mix size	<75 μm	75–125 μm	125–180 μm	>180 μm
3	89.0 ± 0.9	89.0 ± 0.7	87.3 ± 0.7	87.8 ± 0.9	86.8 ± 0.5
5	92.2 ± 0.3	90.3 ± 0.6	90.0 ± 0.5	90.0 ± 0.8	90.8 ± 0.6

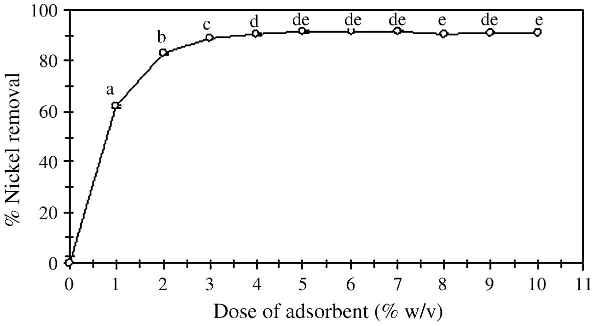

Fig. 5. Effect of adsorbent dosage on nickel removal from electroplating rinse water by coir pith (initial Ni(II) concentration of 145 mg l^{-1}, initial solution pH 3.92).

The experiment determined the efficiency of nickel adsorption by varying the particle size of coir pith. It was found that various particle size of coir pith could not affect nickel adsorption (Table 2). It means that the composition in the various sizes of coir pith is homogeneous. Therefore, a mix of size of coir pith was used in these experiments.

4.3. The adsorption isotherm

The data about nickel adsorption was fitted to the Langmuir and Freundlich isotherms. The equations of Langmuir and Freundlich isotherms are shown in Table 3. The results implied that the correlation coefficients of coir pith fitted the Langmuir and Freundlich isotherms.

The maximum value of nickel adsorption ($q_{\max}$) by coir pith was low. Therefore, coir pith was modified by treatment with NaOH to increase the efficiency of nickel adsorption. This experiment studied the optimum conditions (pH and adsorbent dosage) and found them to be pH 4–7 and 2% (w/v). The affect of solution pH on modified coir pith was similar to coir pith (not modified) in that at pH 2 the efficiency of nickel adsorption decreased because H$^+$ ions compete with nickel for adsorption. The efficiency of nickel adsorption using modified coir pith was 94.5% at 2% (w/v) of dosage. The result shows that modified coir pith increased the efficiency to 94.5% because sodium hydroxide could dissolve impurities [17]. After treatment with sodium hydroxide the functional group of coir pith was changed from carboxylate ($RCOOCH_3$) to RCOO$^-$ [18,19]. Therefore, modified coir pith had more free O$^-$ to bind with nickel ions so the capacity of nickel adsorption by modified coir pith was increased.

Table 3
Isotherm constant of nickel adsorption from electroplating rinse water by coir pith and modified coir pith

Type of isotherm	Adsorbent	
Parameter	Coir pith	Coir pith treated with NaOH
Langmuir		
$q_{\max}$ (mg g^{-1})	9.5	38.9
k_a (l mg^{-1})	0.01243	0.01413
r^2	0.9834	0.9905
Fruendlich		
k_F (mg g^{-1})(l mg^{-1})	1.08	1.14
$1/n$	0.327	0.4441
r^2	0.9825	0.9872

Table 4
Comparison of nickel adsorption capacity (mg g^{-1}) by various adsorbents

Adsorbents	q (mg g^{-1})	Reference
Waste sorbents		
Sugar beet pulp	17.5	[15]
Anaerobic biomass	25	[16]
Grape stalks	30	[7]
Coir pith	9.5	This study
Modified coir pith	38.9	This study

The Langmuir isotherm and the Freundlich isotherm confirmed the layer of adsorbate on adsorbent and Langmuir equation could be finding the maximum capacity of nickel adsorption by the coir pith.

The Langmuir parameters $q_{\max}$ and k_a were determined from the data using a linear least squares program. The Freundlich parameters k_F and $1/n$ (Freundlich constant related to the intensity ($0 < 1/n < 1$)) were calculated from a linear least-squares analysis of the data transformed according to Eqs. (3) and (4). The calculated parameters are summarized in Table 3. The nickel adsorption was fitted to the Langmuir isotherms that showed that the maximum value of nickel adsorption ($q_{\max}$) by coir pith and modified coir pith were 9.5 and 38.9 mg g^{-1}, respectively. In Fruendlich shown k_F and $1/n$ that confirmed the adsorption parameter. It was found that k_F of modified coir pith was higher than coir pith. This isotherm also has the same trend of Langmuir parameter ($q_{\max}$) of coir pith and modified coir pith. The results of r^2 of both isotherms were similar. Therefore, the both isotherms could be use to analyze in this experiment.

Table 4 shows the capacity of nickel adsorption by various adsorbents compared with coir pith and modified coir pith. It was found that modified coir pith has highly efficient nickel adsorption.

4.4. Desorption study

The results of desorption are shown in Table 5. The Ni-adsorbed coir pith in a batch experiment, put into the column,

Table 5
Desorption of the Ni-adsorbed coir pith by distilled water, 0.0125 M H_2SO_4 and 0.025 M H_2SO_4, respectively

Experimental condition	Desorption (%)			Total desorption (%)
	Cycle number (1), distilled water	Cycle number (2), 0.0125 M H_2SO_4	Cycle number (3), 0.025 M H_2SO_4	
Column system	3.9 ± 1.7	90.7 ± 3.6	2.9 ± 1.1	97.1 ± 0.9

Table 6
Nickel removal from electroplating rinse water by the composition of coir pith

Adsorbents	Nickel removal (%)
Coir pith (5%, w/v)	91.2 ± 0.4
Lignin (1.8% in 5%, w/v, of coir pith)	36.6 ± 1.2
Holo-cellulose (2.2% in 5%, w/v, of coir pith)	58.7 ± 1.0

was washed with distilled water to elute the remaining nickel. Then, the sample was desorbed by 0.0125 M H_2SO_4 and 0.025 M H_2SO_4, respectively (Table 5). The percent of Ni(II) desorbed from Ni-adsorbed coir pith by 0.0125 M H_2SO_4 and 0.025 M H_2SO_4 were 90.7 and 2.9%, respectively. From these results, the distilled water can not release nickel and found that sulfuric acid (H_2SO_4) could efficienly elute nickel from the coir pith. Therefore, the Ni(II) ions were replaced by H^+ ions from the sulfuric acid because H^+ ions (electronegativity of $H^+ = 2.20$) are more electronegativity than Ni(II) ions (electronegativity of Ni(II) = 1.91). This implied that nickel adsorption by coir pith involved electrostatic interaction.

4.5. The mechanism of nickel adsorption as confirmed by the coir pith compositions

The mechanism of nickel adsorption was confirmed by the composition of coir pith (lignin, holo-cellulose). Table 6 shows that lignin and holo-cellulose could adsorb nickel in rinse water solution. This experiment used the comparative mass in 5% of coir pith (1.8 % lignin, 2.2% holo-cellulose) and found that the percent of nickel adsorption by lignin and holo-cellulose was 35.6 and 58.7%, respectively. In addition, the efficiency for nickel adsorption by coir pith was 91.2%. Therefore, lignin and holo-cellulose were involved in nickel adsorption.

4.6. Functional groups involved in nickel adsorption

IR spectrum of mixed sizes of coir pith and the composition of coir pith (lignin and holo-cellulose) show the functional groups that are involved in the nickel adsorption (Figs. 1 and 6). Fig. 1 shows that the IR spectra of coir pith and modified coir pith at 3420.00, 1616.00, 1514.00, 1450.00 and 1372.00 cm^{-1} which were shifted to 3321.00, 1604.00, 1509.00, 1423.00 and 1372.00 cm^{-1}, respectively, and show that hydroxyl groups (in carboxylic groups and aromatic rings) were changed. The capacity of nickel adsorption by modified coir pith that involved hydroxyl groups increased. Fig. 1 presents the IR spectra of coir pith (before and after adsorption) at 3420.08, 2935.94 and 562.30 cm^{-1} which were shifted to 3416.02, 2921.32 and 557.90 cm^{-1}, respectively, and that show methoxy and hydroxyl were involved in nickel adsorption. Fig. 1 presents the IR spectra of modified coir pith (before and after adsorption) at 3321.00 and 2129.00 cm^{-1} which were shifted to 3328.00 and 2122.00 cm^{-1}, respectively, and show a hydroxyl group that was involved in nickel adsorption. Fig. 6 presents the IR spectra of lignin (before and after adsorption) at 3417.63 and 535.53 cm^{-1} which were shifted to 3412.35 and 548.00 cm^{-1}, respectively, and show that methoxy and hydroxyl in lignin were involved in nickel adsorption. Fig. 6 presents the IR spectra of holo-cellulose (before and after adsorption) at 3289.00, 2906.00, 1658.00, 1021.00 and 469.00 cm^{-1} which were shifted to 3297.00, 2917.00, 1642.00, 1055.00 and 479.00 cm^{-1}, respectively, and show that hydroxyl groups in holo-cellulose were involved in nickel adsorption.

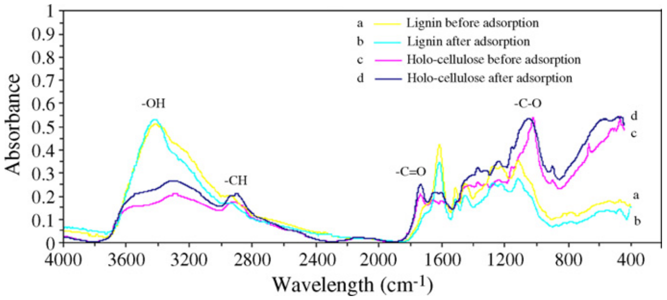

Fig. 6. IR spectra of lignin and holo-cellulose before and after nickel adsorption from electroplating rinse water.

Gardea-Torresdey et al. [19] attempt to promote increased metal binding by the creosote biomass, the biomass was reacted with 0.1 M NaOH so that ester groups might be converted into carboxylate groups. The following chemical reaction that produces carboxylate groups from methyl esters is depicted below:

$$\text{R-COO-CH}_3 + \text{NaOH} \rightarrow \text{R-COO}^- + \text{CH}_3\text{OH} + \text{Na}^+$$

The possible formed carboxylate groups tended to have a much higher metal-binding ability than methyl ester groups (mainly at pH 5).

Table 7 shows modified coir pith found increased free O^- group of OH, RCOOH and $RCOOCH_3$. Therefore, sodium hydroxide increased metal binding site of modified coir pith. These results confirmed that the hydroxyl and methoxy groups (in carboxylic groups and aromatic rings) were involved in nickel adsorption by coir pith.

4.7. Determination of the oxidation number of nickel adsorption by XAS

Fig. 7 shows the oxidation number of nickel in coir pith and modified coir pith (after adsorption) are nickel ions(II) when

Table 7
Band characteristics of FTIR spectra related to transformation (coir pith → modified coir pith) by NaOH treatment[a]

Characteristics	υ (cm^{-1}) related to the crystal system		υ (cm^{-1})/absorbance change	Assignment	Reference
	Coir pith	Modified coir pith			
Peak shift	3417	3313	−104/▼	γOH (hydrogen bonded)	[20]
	2916	2933	+17/▲	γCH	[20]
	1732	1722	−10/▲	γC=O	[7]
	1621	1608	−13/▲	γC=O	[7]
	1447	1426	−21/▲	δCH_2 (sym) at C-6	[20]
	1050	1063	+13/▲	δCO at C-6	[7,20]
	771	777	+6/▲	δCOH out-of-plane (cellulose)	[20]
	515	518	+3/▲	δCOH out-of-plane (cellulose)	[20]
Absorbance change					
	1514	1514	▲	γCCH	[7,20]
	1372	1372	▲	γCH	[20]
	1325	1325	▲	δCH_2 (wagging) at C-6	[20]
	1265	1265	▲	δCOH in plane at C-2 or C-3	[20]
	1157	1157	▲	γCOC at β-glucosidic linkage	[20]
	1103	1103	▲	γCOC at β-glucosidic linkage	[20]
	895	895	▲	γCOC at β-glycosidic linkage, γCOC, γCCO and γCCH at C-5 and C-6	[20]

[a] Key to symbols: γ, stretching; δ, bending; ▲, increase; ▼, decrease.

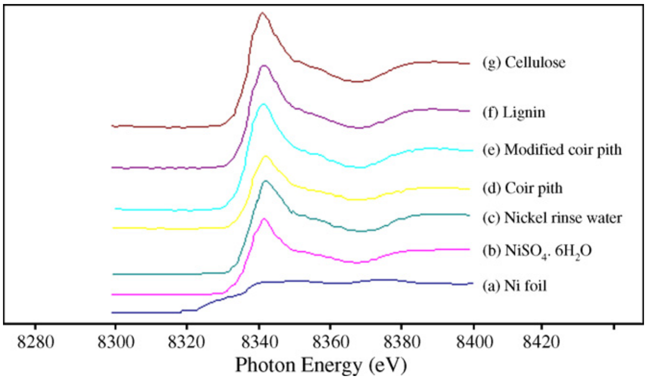

Fig. 7. XANES spectra of nickel standard and adsorbents such as (a) nickel foil, (b) $NiSO_4 \cdot 6H_2O$, (c) nickel rinse water, (d) coir pith, (e) modified coir pith, (f) lignin and (g) holo-cellulose.

compared with standard nickel (oxidation number Ni(0) and Ni(II)) [21–22].

5. Conclusions

Coir pith was suitable to adsorb nickel from electroplating rinse water. The advantages of this adsorbent were low cost, availability in high quantities and high adsorption capacity. Variables that affected nickel adsorption involved the conditions of adsorption such as pH, contact time, temperature and dosage. However, coir pith was adsorbed with a low efficiency. Therefore, coir pith was modified with NaOH to increase nickel adsorption from 9.5 to 38.9 mg g^{-1} coir pith. Sodium hydroxide increased metal binding site (free O^{-}) of modified coir pith. The mechanism of nickel adsorption by coir pith was chemisorption and was confirmed by desorption with acid. The components of coir pith such as lignin and holo-cellulose were involved in nickel adsorption. In addition, functional groups that were involved in nickel adsorption were hydroxyl and methoxy groups. It was confirmed by XAS that the oxidation number of nickel in nickel adsorption by coir pith and modified coir pith was Ni(II).

Acknowledgement

The authors would like to thank the Royal Golden Jubilee scholarship, the Thailand Research Fund for providing the research funds.

References

[1] A.J. Pedersen, Characterization and electrolytic treatment of wood combustion fly ash for the removal of cadmium, Biomass Bioenerg. 25 (4) (2003) 447–458.
[2] A. Baran, E. Bıak, S. Hamarat Baysal, S. Onal, Comparative studies on the adsorption of Cr(VI) ions on to various sorbents, Bioresour. Technol. 98 (2006) 661–665.
[3] A.H. Elshazly, A.H. Konsowa, Removal of nickel ions from wastewater using a cation-exchange resin in a batch-stirred tank reactor, Desalination 158 (1–3) (2003) 189–193.
[4] V.W.D. Chui, K.W. Mok, C.Y. Ng, B.P. Luong, K.K. Ma, Removal and recovery of copper(II), chromium(III), and nickel(II) from solutions using crude shrimp chitin packed in small columns, Env. Int. 22 (4) (1996) 463–468.
[5] T. Vengris, R. Binkien, A. Sveikauskait, Nickel, copper and zinc removal from waste water by a modified clay sorbent, Appl. Clay Sci. 18 (3–4) (2001) 183–190.
[6] S. Pradhan, S.S. Shukla, K.L. Dorris, Removal of nickel from aqueous solutions using crab shells, J. Hazard. Mater. 125 (1–3) (2005) 201–204.
[7] I. Villaescusa, N. Fiol, M. Martínez, N. Miralles, J. Poch, J. Serarols, Removal of copper and nickel ions from aqueous solutions by grape stalks wastes, Water Res. 38 (4) (2004) 992–1002.
[8] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coirpith, Sep. Purif. Technol. 24 (3) (2001) 497–505.
[9] S. Erdoğan, Y. Önal, C. Akmil-Başar, S. Bilmez-Erdemoğlu, Ç. Sarıcı-Özdemir, E. Köseoğlu, G. İçduygu, Optimization of nickel adsorption from aqueous solution by using activated carbon prepared from waste apricot by chemical activation, Appl. Surf. Sci. 252 (5) (2005) 1324–1331.

[10] E.A. Oliveira, S.F. Montanher, A.D. Andrade, J.A. Nóbrega, M.C. Rollemberg, Equilibrium studies for the sorption of chromium and nickel from aqueous solutions using raw rice bran, Process Biochem. 40 (11) (2005) 3485–3490.

[11] A. Sharma, K.G. Bhattacharyya, *Azadirachta indica* (Neem) leaf powder as a biosorbent for removal of Cd(II) from aqueous medium, J. Hazard. Mater. 125 (1–3) (2005) 102–112.

[12] S.R. Shukla, R.S. Pai, Comparison of Pb(II) uptake by coir and dye loaded coir fibres in a fixed bed column, J. Hazard. Mater. 125 (1–3) (2005) 147–153.

[13] G.H. Pino, L.M.S.D. Mesquita, M.L. Torem, G.A.S. Pinto, Biosorption of cadmium by green coconut shell powder, Miner. Eng. 19 (5) (2006) 380–387.

[14] C. Namasivayam, M.D. Kumar, K. Selvi, R.A. Begum, T. Vanathi, R.T. Yamuna, 'Waste' coir pith—a potential biomass for the treatment of dyeing wastewaters, Biomass Bioenerg. 21 (6) (2001) 477–483.

[15] Z. Reddad, C. Gérente, Y. Andrès, M.C. Ralet, J.-F. Thibault, P.L. Cloirec, Ni(II) and Cu(II) binding properties of native and modified sugar beet pulp, Carbohydr. Polym. 49 (1) (2002) 23–31.

[16] A.H. Hawari, C.N. Mulligan, Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass, Bioresour. Technol. 97 (4) (2006) 692–700.

[17] S. Borysiak, B. Doczekalska, Influence of chemical modification of wood on the crystallisation of polypropylene, Holz als Roh- und Werkstoff. 64 (2006) 451–454.

[18] J.O. Karrisons, M. Anderssons, P. Berntssons, T. Chihani, P. Gatenholm, Swelling behavior of stimuli-responsive cellulose fibers, Polymer 39 (16) (1998) 3589–3595.

[19] J.L. Gardea-Torresdey, A. Hernandez, O. Rodriguez, K.J. Tiemann, S. Sias, Enhanced metal-binding capacity of NaOH treated *Larrea tridentata* leaf tissue, in: Proceedings of the 1998 Conference on Hazardous Waste Research, (1998) pp. 101–110.

[20] S. Youn Oh, D.I. Yoo, Y. Shin, H. Chul Kim, H. Yong Kim, Y. Sik Chung, W. Ho Park, J. Ho Youk, Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy, Carbohydr. Res. 340 (2005) 2376–2391.

[21] I. Dékány, F. Szántó, L.G. Nagy, Selective liquid adsorption and structural properties of montmorillonite and its hexadecylpyridinium derivatives, Colloid Polym. Sci. 256 (2) (1978) 150–160.

[22] S. Cetin, E. Pehlivan, The use of fly ash as a low cost, environmentally friendly alternative to activated carbon for the removal of heavy metals from aqueous solutions, Colloids Surf. A: Physicochem. Eng. Aspects 298 (2007) 83–87.