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24**Chemical Engineering Journal** 172 **(2011)** 158–166 **Contents lists available at ScienceDirect Chemical Engineering Journal journal homepage: www.elsevier.com/locate/cej** Evaluation **of**

5**cassava peel waste as lowcost biosorbent for Ni-sorption: Equilibrium, kinetics, thermodynamics and mechanism Alfin** Kurniawana, **Aline Natasia** Kosasiha,b, **Jonathan**

Febriantoa,

6**Yi-Hsu Jub,** Jaka Sunarsoc, **Nani Indraswatia, Suryadi Ismadjia,∗ a Department of Chemical Engineering, Widya Mandala Catholic University, Kalijudan 37, Surabaya 60114, Indonesia b Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Sec. 4, Keelung Rd., Taipei** 10607, **Taiwan**

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16**Australian Research Council (ARC) Centre of Excellence for Electromaterials Science, Institute for Technology Research and Innovation, Deakin University, 221 Burwood Highway, Victoria 3125, Australia**

33**article info Article history: Received** 1 **April 2011 Received in revised form** 23 **May 2011 Accepted 24 May 2011**

Keywords: Cassava peel Isotherm Nickel Biosorption abstract The feasibility of cassava peel waste for Ni-sorption is evaluated in this work. The biosorbents are characterized by Boehm titration, Fourier transform-infra red (FTIR) spectroscopy, Nitrogen sorption, scanning electron microscopy-energy dispersive X-ray (SEM-EDX) analysis (e.g. elemental

21**mapping) and X-ray photoelectron spectroscopy (XPS).** Adsorption **experiments**

are performed in batch mode at

35**30 ◦C (303.15 K),** 45 ◦**C** (318 **.15 K)**

and 60 ◦C (333.15 K). The performance of several temperature dependence forms of isotherm models e.g. Langmuir, Freundlich, Sips and Toth to represent the adsorption equi- librium data is evaluated and contrasted. Sips model demonstrates the best fitting with the maximum uptake capacity for Ni(II) ions of 57 mg/g (0.971 mmol/g) at pH 4.5. For kinetic data correlation,

39**pseudo- second order model** shows **the best** representation. **The**

chemisorption mechanism and thermodynamics aspect are also discussed. © 2011 Elsevier B.V. All rights reserved. 1.

10**Introduction Water pollution by heavy metals is a serious environmental problem with harmful impacts** to **ecological balance and living organisms, including humans** due **to** their toxicity, accumulation in food chain and persistence nature. Nickel is one type of heavy metals generated from various industrial effluents such as metal electroplating, mining and extractive metallurgy, battery and accu- mulator industries, pigment as well as alloy and petroleum refinery [1]. Nickel possesses carcinogenic and mutagenic properties along with its acute and chronic effect which can cause several disor- ders and diseases like nausea, vomiting, skin dermatitis, infertility, apathy, chronic headache, lung, kidney, liver, intestine and heart malfunction [2]. This heavy metal is considered as hazardous sub- stance; hence its removal from wastewater forms an essential effort in the protection of environment and water resources. A large variety of wastewater treatment methods for nickel are available which include chemical precipitation, ion exchange, membrane filtration, coagulation and flocculation, flotation, elec- trochemical treatment and adsorption [3]. However, most are ineffective due to low removal efficiency and high treatment cost for low contaminant concentrations. Adsorption is known as a ∗ Corresponding author. Tel.: +62 313891264; fax: +62 313891267. E-mail addresses: suryadiismadji@yahoo.com, suryadi@mail.wima.ac.id (S. Ismadji).

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05.083 promising technique for this purpose due to its selectivity, high effi- ciency, low operational cost and minimal amount of toxic sludge. Nowadays, there are great interests to find potential and alterna- tive adsorbents from agricultural by-products and forestry wastes [4] to overcome the limitation use of commercial adsorbents such as activated carbon for industrial applications. Abundant amount of non-used cassava peels in Indonesia (approximately 440,800 ton peels are produced in 2009) fits this purpose and might

32**be utilized as an** effective and **low cost biosorbent.** Recently, **the** utilization **of**

this agricultural waste as alternative adsorbent for Cu(II) removal has been studied [5]. The aim of the present study is to explore the various aspects of Ni-sorption onto cassava peel, which include its equilibrium, mech- anism, kinetics and thermodynamics. The temperature dependence forms of several adsorption isotherm models are adopted to cor- relate adsorption equilibrium data. In our previous studies, these particular models have been successfully applied

18**to evaluate** the **adsorption equilibrium data of**

several organic compounds onto organo-clay [6,7].

18**2. Materials and methods 2.1. Chemicals**

NiSO4·6H2O (A.R. Grade; Wako Pure Chemical Industries, Ltd, Taiwan) was used as metal ion source.

27**2.2. Preparation of biosorbent** Cassava **peel waste was collected from**

a cassava starch factory located near Surabaya, East Java, Indonesia. The collected cassava peels were washed repeatedly with tap water to remove sand and surface dirt. Subsequently, the peels were dried under the sunlight for 48 h before dried further in an oven at 100 ◦C for 24 h. The cas- sava peels were then crushed using micro-hammer mill (JANKE and KUNKEL) and sieved to certain particle sizes (125–177 ?m, 177–250 ?m, 250–500 ?m). The final product was finally kept in airtight plastic bags for further use. 2.3. Characterizations of biosorbent 2.3.1. Boehm titration The oxides on the surfaces of the adsorbent were analyzed by Boehm titration method [8]. The procedure is as follows: a fixed amount of cassava peel (0.5 g) was added into several conical flasks containing 50 cm3 of 0.05 N: Na2CO3, NaHCO3, HCl and NaOH solu- tion. Subsequently, the flasks were placed into the thermostatic bath-shaker (Memmert UM400) and shaken at room temperature for 48 h. The mixture was then decanted and filtered through using Whattman 42 filter paper, in which

11**10 cm3 of the remaining** solu- tion **was titrated** using **0.05** N **HCl or NaOH; depending on the original solution used. The** amount **of** acid surface **groups was** cal- culated under **the assumptions that NaOH neutralizes carboxylic,** phenol **and** lactone;

17**Na2CO3 neutralizes** lactone **and** carboxylic; **NaHCO3 neutralizes only carboxylic. The** number **of basic** surface groups **can be determined from the** amount of **HCl,** which reacted **with**

sample. 2.3.2. Fourier transform-infra red (FTIR) The surface functional groups of adsorbent were analyzed by FTIR spectroscopy, conducted in FTIR Shimadzu 8400S using KBr disk technique. The spectra data of the sample were collected in the mid-IR wavenumber range (500–4000 cm−1). 2.3.3. Nitrogen sorption The pore structure of the adsorbent was characterized by N2 sorption using a gas sorption analyzer (Quadrasorb SI) at 77.15 K. Prior to the adsorption analysis, the sample was degassed in a vacuum condition at 423.15 K for at least 24

8**h. The** standard **Brunauer–Emmett–Teller** (BET) equation **was** used **to** calculate **the** specific BET **surface area** (SBET) **of the sample**

in the relative pres- sure (P/P0)

37**range from 0.06 to 0.3. The** total **pore** volume **of** the sample was **determined from** the N2 **adsorption–** desorption **data** at **the**

highest relative pressure (P/P0 = 0.994).

14**2.3.** 4. **Scanning electron** microscopy **(SEM) The surface morphology of the** adsorbent **was** visualized in **a**

7**JEOL JSM-6400F field emission** SEM. **The**

SEM sample was coated with a thin layer of platinum to make them electronically conduc- tive. The sputter-coater

12**(Eiko IB-5)** was **operated at 6 mA for** 4 **min in** an **argon atmosphere. The coated** sample was **then placed in the SEM specimen chamber and scanned at an** electron acceleration **voltage of 10 kV,**

7**spot size of 8, aperture of 4 and** 37 mm **working distance. 2.3.**

5. Energy dispersive X-ray (EDX) and X-ray elemental mapping The EDX spectra and X-ray elemental mapping of the metal- loaded adsorbent were obtained using a JEOL JSM-6460 LA low vacuum analytical SEM equipped with EDX-spectrometer. Prior to the analysis, the sample was coated with carbon fiber using a custom-made carbon coater.

20**Acquisition conditions on the SEM were 20 kV, 10 mm working distance and 30 s live time acquisition at approximately 10–15% dead time.**

The X-ray data of the sample were recorded and analyzed using integrated JEOL analysis station (v3.2) software. 2.3.6. X-ray photoelectron spectroscopy (XPS) The XPS spectra of the metal-loaded adsorbent were obtained with a Kratos Axis ULTRA X-ray Photoelectron Spectrometer using

23**monochromatic Al K? X-** ray radiation **(1486.6 eV) at** 150 **W (15 kV, 15 mA). Survey scans were** collected **at** binding **energy** range **of** 0–1200 **eV** with the pass energy adjusted to 160 eV and narrow high-resolution scans at 20 eV. Survey scans were run

3**with 1.0 eV steps and** 100 ms **dwell time** while **narrow high-resolution scans were run with 0.05 eV steps and 250 ms dwell time. Base** pres- sure **in the analysis chamber was 1.0 × 10−9 Torr and during sample analysis was 1.0 × 10−8 Torr.**

2.4. Biosorption experiments The stock solution of NiSO4·6H2O at initial concentration of 200 mg/L was used as synthetic effluent. This solution was pre- pared by dissolving a fixed amount of NiSO4·6H2O into 1 L deionized water. The biosorption equilibrium experiments were conducted by adding various mass of adsorbents (0.1–10 g) into several con- ical

32**flasks containing** 100 **mL of metal solution.** Subsequently, the flasks **were** placed in **a**

thermostat orbital shaker incubator LM- 570 and heated from room temperature to the desirable operating temperature (30 ◦C, 45 ◦C, 60 ◦C). The shaker was then set to rotate at 200 rpm within 2–3 h to reach equilibrium. The metal solution was then centrifuged (Hettich Zentrifugen EBA-20) at 4000 rpm for 5 min to remove solid particles. The residual Ni-metal concen- tration in solution was analyzed using a flame atomic absorption spectrophotometer (Shimadzu AA6200) at = 232.7 nm. For biosorption kinetics, the experiments were carried out as fol- lows: 100 mL of metal solution at initial concentration of 200 mg/L was mixed with 0.5 g of adsorbent with certain particle size in sev- eral conical flasks. The flasks were then placed in an orbital shaker incubator and shaken at 60 ◦C and 200 rpm for certain period of time. During the experiments, at certain interval of time, 10 mL of metal solution was taken from the flasks, centrifuged and ana- lyzed its residual nickel metal concentration. The effect of pH was also studied at pH range of 1.0–9.0. To adjust pH, an appropriate amount of 0.1 N HCl or NaOH solutions was added. All experiments were carried out in triplicate with their averages used as the result. The uptake capacity of cassava peel, in the unit concentration of mmol/g

30**can be calculated** using **following mass balance equation: qe** = (C0 − **Ce) m ×V (1) where qe is the amount of**

metal uptake at equilibrium condition (mmol/g), C0 and Ce is a symbol represented the initial and equi- librium concentration of metal ions in solution (mmol/L), m

9**is the** biosorbent **dose (g) and V is the volume of** metal **solution (L). 3. Results and discussion 3.1.** Characterizations **of**

pristine cassava peel The surface morphology of cassava

27**peel is** depicted **in Fig. 1. Fig. 1** features **the**

non-porous, heterogeneous and complex nature of cassava peel surface. The N2 sorption analysis (Fig. 2) is consis- tent with the SEM result. The specific BET surface area (SBET) of this peel is 3.72 m2/g with N2 sorption capacity of 20.2 cm3/g (STP). Low SBET value is likely due to the low porosity on the material surface [9–11]. The presence of surface oxides in cassava peel can be detected by Boehm titration. The cassava peel surface is mainly Fig. 1. SEM micrographs of cassava peel at two magnifications (a) 600× and (b) 5000×. occupied by acidic groups (0.526 meq/g) and small amount of basic groups (0.108 meq/g). 3.2. Characterizations of Ni-loaded cassava peel 3.2.1. FTIR spectroscopy FTIR can be used to collect information regarding the vibra- tional frequency changes of functional groups, which are involved during sorption process. Fig. 3 presents the FTIR spectra of both pristine and Ni-loaded cassava peel for direct comparison. Fig. 3 demonstrates that cassava peel exhibits heterogeneous and com- 30 Cassava peel adsorption 25 Cassava peel desorption 20 ads (cm3/g) 15 V 10 5 0 0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 Relative pressure (P/P0) Fig. 2. N2 adsorption–desorption isotherm of cassava peel at 77 K. 0.50 0.45 Cassava peel Cassava peel + Ni(II) ions 0.40 C-O (COO-Ni) 0.35 Absorbance 0.30 0.25 0.20 0.15 O-H bend

36**C-H stretch C=N stretch C=C stretch C=O stretch C-O stretch**

0.10 0.05 0.00 4000 3500 3000 2500 2000 1500 1000 500 Wavenumber (cm-1) Fig. 3. FTIR spectra of pristine and Ni-loaded cassava peel. plex surface with various functional groups appearing at certain wavenumber (Table 1). The alteration of several functional groups in pristine cassava peel after metal sorption was evidenced. The FTIR spectra of Ni-loaded cassava peel reveal that the alter- ation of absorption peaks (3620, 1340 and 942 cm−1) occurs after metal sorption. The peak observed at 3620 cm−1; corresponds to O–H stretch of hydroxyl groups in the lignocellulosic structure dis- appears (after sorption). Modification of another peak (at 942 cm−1 associated with the decrease of peak energy for O–H bend in car- boxylic acid) is also observed due to their involvement during Ni-sorption. Moreover, the existence of new peak is also noticed at 1340 cm−1; representing C–O stretch of metal–carboxylate (COO–M) groups. Overall, change in the surface functional groups of the adsorbents is mainly observed in hydroxyl and carboxyl groups; denoting that their deprotonated forms (hydroxylate and carboxy- late anions) are the adsorption sites for Ni(II) [12,13]. 3.2.2.

21**Energy dispersive X-ray (EDX), X-ray** elemental **mapping and X-ray** photo electron **spectroscopy (XPS)**

analyses The presence of heavy metal after sorption can be detected by analyzing the adsorbent surface using SEM-EDX, X-ray elemental mapping and XPS analyses. EDX is an analytical technique to iden- tify the element presence on the material surface based on their characteristic X-ray energy. This technique is normally coupled with SEM analysis to gain more complete result. The SEM-EDX spectra of Ni-loaded cassava peel are given in Fig. 4. In Fig. 4, Ni(II) ions' presence can be detected from the Ni–L and Ni–K peaks, which appear in the binding energy range of 0.85–0.87 keV and 7.5–8.3 keV, respectively. The X-ray elemental Table 1 Functional groups of pristine and Ni-loaded cassava peel. Functional group Wavenumber (cm−1) Pristine Ni-loaded O–H bend (carboxylic acids) C–O stretch of –OCH3 groups (lignocelluloses compound) C–O stretch of metal–carboxylate complex (COO–Ni)

31**C–C stretch** (aromatics structure) **C O stretch** (asymmetric COO) **–C C– stretch** (alkenes) **C** N **stretch** (nitrile groups) **C–** H **stretch** (alkanes) **C–** H **stretch** (methylene groups) **O–** H **stretch**

(lignocelluloses structure) 942 1050 – 1515 1636 1764 2378 2847 2941 3602 940 1052 1340 1514 1637 1762 2377 2846 2943 – Fig. 4. SEM-EDX spectra of Ni-loaded cassava peel. Fig. 5. SEM and X-ray elemental mapping of Ni-loaded cassava peel. mapping is also performed to measure qualitatively the distribution

39**of metal ions on the adsorbent surface** (Fig. **5).**

In Fig. 5, nickel metal is represented by the bright region. The XPS spectroscopy of Ni- loaded cassava peel is recorded to gain insight into metal–surface interaction in the sorption study. Fig. 6 displays the XPS spectra of Ni-loaded cassava peel. In this figure, the presence of Ni(II) ions is verified from the assignment of Ni 2p3/2 XPS spectra, which appear at binding energy of 854.6 eV; representing Ni2+ in the oxide state. Fig. 6. XPS spectra of Ni-loaded cassava peel. Fig. 7. Effect of pH on the Ni(II) ions equilibrium uptake (C0 = 200 mg/L, biosorbent mass = 1.5 g, T = 45 ◦C). 3.3. Effect of pH The pH is a key factor that should be considered in the sorption since it substantially affects the mechanism of

19**metal ion** uptake. **The effect of** pH on the **Ni(II) ion** uptake at equilibrium **was studied by varying**

pH from 1 to 9. Fig. 7 shows that the amount of Ni(II) ion uptake increases steadily by increasing pH from 1 to 4 and reach its maximum at pH 4.5. At higher pH, the amount of Ni(II) adsorbed is less compared to that at pH 4.5. This phenomenon might be caused by the formation of metal hydroxide [Ni(OH)2], which takes place at alkali pH range (pH > 7). The formation of Ni(OH)2 reduces the

8**concentration of Ni(II) ions in the solution;** hence **the**

38**percentage removal of Ni(II) by**

cassava peel also decreases. For this reason, pH 4.5 was selected during metal biosorption experiments and serves also as optimum value for Ni(II) removal. Low nickel uptake in acidic solution might be due to the com- petition between Ni(II) ions and H3O+ ions for the adsorption sites, which reduced the amount of Ni(II) uptake. The presence of H3O+ ions also retards the Ni-sorption due to repulsion force between protonated adsorbent surface and metal cations. This phenomenon can be explained on the basis of carboxylic groups (R–COOH) being protonated by H3O+ ions as follows: R–COOH + H3O+ → R–COOH2+ + H2O (2)

17**As the pH** increase, **the concentration of** H3O+ ions in **metal**

solu- tion decreases and the repulsion between adsorbent and adsorbate also weakens; resulting in the increase amount of adsorbed metal ions (onto the solid surface). Increasing pH also exposes more nega- tively charged ligands such as carboxylate anions (R–COO−) on the adsorbent surface due to the dissociation of carboxylic at pH range of 3.5–5.5 [14], leading to the electrostatic attraction

8**of Ni(II) ions onto** these **groups.**

3.4. Chemisorption

8**of Ni(II) ions onto** cassava peel **surface** The chemisorption mechanism **of**

Ni(II) ions onto cassava peel surface was proposed in this study using molecular simulation by ChemDraw software package. Some information about the surface chemistry characterization of the adsorbents, for example the alter- ation of functional groups can be used as evidences in proposing biosorption mechanism. The Ni-chemisorption mechanism onto cassava peel surface and the molecular model of Ni–carboxylate complex is illustrated in Fig. 8. In Fig. 8, it can be seen that Ni(II) ions were bound into car- boxylate groups in the lignocellulosic structure of cassava peel by creating ionic forces with carboxylic oxygen atoms. These oxy- gen atoms exhibited negative charge in their structure as a result of the dissociation of carboxylic groups. The negatively charged oxygen atom in carboxylate anions will coordinate with nickel cations, resulting in the formation of metal–carboxylate complexes (COO–Ni) on the cassava peel surface. The presence of metal–carboxylate complex could be also indi- cated from the peak at 1340 cm−1, which assigned to C–O stretch of COO–Ni groups. Other phenomena were also observed during the formation of COO–Ni complex, relating to the disappearance of O–H stretch at 3600 cm−1 and reduction of peak energy for O–H bend at 940 cm−1. This statement was in agreement with FTIR results as shown in Fig. 3. In addition, the coordination type of metal–carboxylate com- plexes can also be determined by examining the vibrational modes of vasym (COO−) and vsym (COO−) in the wavenumber region of 1300–1750 cm−1. As reported by Papageorgiou et al. [15] that the unidentate coordination of metal–carboxylate complex occurs where the difference (?v) between vasym (COO−) and vsym (COO−) is larger than 200 cm−1. In this study, the ?v (COO−) value was 297 cm−1, suggested the formation of Ni–carboxylate complex through unidentate chelating coordination. 3.5. Biosorption isotherms Biosorption isotherm is vital information from the view of prac- tical design and operation of the sorption system as it describes the distribution of adsorbates among solid and liquid phases at equi- librium. In this work, several temperature dependence forms of

18**isotherm models (Langmuir,** Freundlich, **Sips and** Toth) **were used to** represent **adsorption equilibrium data.**

The Langmuir model can be expressed as follows: qe = qm KL(T) × Ce 1 + KL(T) × Ce (3)

14**where qm is the** Langmuir based **maximum adsorption capacity** for particular **adsorbent** (mmol **/g) and KL is Langmuir**

parameter that defined as affinity constant at equilibrium (L/mmol). The tem- perature dependence form of qm parameter, which proposed by Dubinin–Radushkevich and KL is given as follows [16,17]: q m = q0 exp(ı(T − T0)) (4) KL(T)=K0 exp Qads (5) RT where q0

5**is the maximum** uptake **capacity** of adsorbate **at reference ( ) temperature**

T0 (298.15 K), ı is a parameter representing thermal expansion coefficient of adsorbate (K−1), Qads is heat of adsorption

25**(kJ/mol), R is the** universal **gas constant (8.314 J mol−1 K−1) and** K0 **is the adsorption** affinity at reference **temperature** T0 (L/mmol). **The**

28**essential characteristic of Langmuir** model **can be expressed by dimensionless constant called equilibrium parameter, RL,** which **defined** as: **RL = 1 + KLC0**

1 (6)

22**The value of RL indicates** various characteristics **of** adsorption **isotherm to be irreversible (RL = 0), linear (RL = 1),** unfavorable **(RL > 1)** and favorable **(0 < RL < 1). The**

second adsorption model is Freundlich. This model was proposed by Freundlich (1932) assuming that the adsorbent surface is heterogeneous with uneven distribution of adsorption heat and affinity over the solid surface. Although Freundlich model has widely applied in many sorption studies, it has a limitation in correlating equilibrium data at wide concentration range since this isotherm

4**does not have a proper Henry law** limit **at low**

Fig. 8. Ni-chemisorption mechanism and the model of Ni–carboxylate complex.

4**concentration and does not have a** saturation **limit** at high-end **concentration.**

The Freundlich model

34**has the following form: qe** = KF (T) × Ce1 **/n**

(7) where n and KF are the Freundlich parameters which rep- resent the system heterogeneity and adsorption capacity [(mmol/g) (mmol/L)−n], respectively. The parameter KF and n can be expressed as the temperature dependence form as follows [16]: ¸RT KF = KF0 exp − A (8) 0 1 ( ) n = RT A0 (9) The third adsorption model is Sips. Sips (1948) proposed an empirical equation describing adsorption behavior in heteroge- neous system which has similar form to Langmuir model: qe = qm (Ce × KS (T))1/n (10) (1 + (Ce × KS (T))1/n) The temperature dependence forms of Sips parameter are [16]: KS = KS0 exp RT0((TQ/aTd0s) − 1) (11) [ ] n= 1 (1/n0) + (1 − (T/T0)) (12) where KS0 and n0 is the adsorption affinity and the system het- erogeneity parameter at reference temperature T0 (298

5**.15 K),** respectively **and is a constant parameter. The**

last adsorption model is Toth. The Toth model is one of the most popular three-parameter adsorption equations used in pre- dicting adsorption phenomena in heterogeneous system due to its capability to overcome the drawback of Sips and Freundlich model. The Toth model has the form: qe = qm bT(T) × Ce (1 + (bT(T) × Ce)t)1/t (13) Here t and bT are the Toth parameter characterizing the system het- erogeneity and the biosorption affinity (L/mmol), which is specific for adsorbent–adsorbate system. The parameter bT and t in Toth model can be expressed as temperature function [16]: bT = b0 exp QRaTd0s T0 − 1 T (14) [( )] t = t0 + 1 − T (15) T0 where b0 and t0 are the adsorption affinity and t parameter at ref- ( ) erence temperature T0 (298

5**.15 K) and is a constant parameter. The**

Ni-sorption equilibrium data at three different tempera- tures e.g.

35**30 ◦C (303.15 K),** 45 ◦**C** (318 **.15 K)** and 60 ◦C (333.15 K) and the fitting of isotherm models are shown in Fig. 9. The isotherm parameters were calculated by nonlinear regression method (Table 2). Fig. 9 shows that all models could fit the adsorp- tion equilibrium data well (R2 > 0.998), however, to assess the applicability and suitability of the models in correlating experi- mental data, the

4**physical meaning of each parameter** should be examined. **The parameter**

q0, which represents the maximum uptake capacity of adsorbent at temperature T0, refers to the complete monolayer coverage. Table 2 demonstrates that the values of q0 parameter for Langmuir, Sips and Toth models are similar. These parameter values correspond to the Ni(II) ion uptake around 57 mg/g. Therefore, the value of q0 parameter in Langmuir, Sips and Toth is reasonable and consistent. For comparison purpose, the maximum biosorption capacity of several adsorbents for Ni(II) Fig. 9. Ni-sorption equilibrium data and the fitting of temperature dependence forms of isotherm models (C0 = 200 mg/L, particle size = 125–177 ?m, pH = 4.5). ion removal is also given in Table 3. The maximum uptake capac- ity (indicated by KF0) from Freundlich model is significantly larger (192.5 mg/g) than that from other models. For non-treated biosor- bent, the obtained maximum uptake capacity value is not possible; hence this model is not discussed further. Table

4**2 The fitted temperature dependence parameters of**

isotherm models for Ni-sorption onto cassava peel. Isotherm model Parameter Value R2 Langmuir q0 (mmol/g) ı (1/K) K0 (L/mmol) Qads (kJ/mol) Freundlich KF0 [(mmol/g) (mmol/L)−n] ¸/A0 (mol/J) Sips q0 (mmol/g) ı (1/K) KS0 (L/mmol) Qads (kJ/mol) n0 Toth q0 (mmol/g) ı (1/K) b0 (L/mmol) Qads (kJ/mol) t0 0.972 0.00628 2.614 × 10−6 40.17 3.279 3.416 × 10−4 0.989 0.00607 2.246 41.03 1.159 4.637 0.981 0.00619 1.835 40.64 3.129 14.473 0.9982 0.9991 0.9987 0.9989 Further verification was performed onto K0, KS0 and b0 param- eters, which is defined as adsorption affinity. K0, in particular, this parameter measures how strong the interaction force between adsorbate molecule and adsorbent surface. Both adsorption affini- ties of Sips and Toth models are comparable to values reported for other sorption systems, however the fitting value of parameter K0 in Langmuir model is considerably low and not consistent with the value reported on most sorption systems. Table 3 The maximum sorption capacity of various adsorbents for Ni(II) removal. Adsorbent Operating condition q m (mg/g) Reference pH T (K) Cashew nut shell Orange peel OPAA – modified orange peel Pomegranate peel Sargassum muticum Gracilaria caudata Pine bark H3PO4 – treated rice bran Acid – treated peepal leaf Barley straw Moringa oleifera bark Cassava peel 5 303.15 5.5 303.15 5.5 303.15 – 318.15 3 293.15 5 293.15 8 – 6 303.15 7 – 4.85 296.15 6 323.15 4.5 – 18.87 9.82 162.6 69.4 70.0 45 12.15 102 6.35 35.8 30.38 57 [22] [12] [12] [23] [24] [24] [25] [26] [27] [28] [13] This study Fig. 10. Ni-biosorption kinetic data and the fitting of kinetic models (C0 = 200 mg/L, T = 60 ◦C, biosorbent mass = 0.5 g, pH = 4.5). The last verification of the physical meaning of the remaining isotherm models (Sips and Toth) is on the n0 or t0 parameter, which represents the heterogeneity of the system. If its value deviates

4**away from unity, the** sorption **system is** considered **more** hetero- geneous. **The value of**

t0 in Toth model is usually less than unity while the n0 parameter in Sips model is greater than unity [16]. Sips model provide reasonable parameter value while Toth model gives incorrect value (Table 2). Thus, Sips model provides the best representation on the exper- imental data. The chemisorption nature of Ni-sorption is also supported by Sips model on which the Qads value lies between 40 and 400 kJ/mol. 3.6. Biosorption kinetics In order to investigate the potential rate-controlling step involved, two

9**kinetic models** namely **pseudo-first order and pseudo-second order were** used to evaluate **kinetic data. The pseudo-first order,**

which is also known as Lagergren equation can be expressed as follows [18]: qt = qe(1 − exp(−k1t)) (16)

7**while the pseudo-second order model** [19] **has the form**

as described in Eq. (17): qt = k2q2et (17) 1 + k2qet

29**where qt and qe** is **the** amount **of** Ni(II) **ions** adsorbed **at time t and equilibrium** condition (mmol **/g), respectively. The rate constant** of k1 (1 **/min)**

and k2 (g/(mmol min)) was attributed to pseudo-first order and pseudo-second order model, respectively and t is time (min). The plot of the experimental data and the model fitting are illustrated in Fig. 10. The kinetic parameters

7**obtained by non-linear regression method are** tabulated in Table **4.**

Table 4 shows that particle size has significant effect to the rate constant (k) and nickel equilibrium uptake (qe). Smaller particle size increases the rate constant and nickel equilibrium uptake to the extent that the equilibrium condition is achieved faster. Smaller particles also provide larger surface area and more available bind- ing sites for Ni(II) ions onto their surface; leading to faster metal ion uptake. Comparing

19**the correlation coefficient (R2)** value, **the pseudo- second order** is better **than** the **pseudo-first order**

model. In addition, the qe parameter in pseudo-second order model provides closer value to the experimental results. These facts suggest

10**that the** potential **rate-** controlling **step in** Ni **-sorption is chemisorption**

involving cation exchange reaction between adsorbate and adsor- bent, surface complexation, coordination and/or chelation. 3.7. Thermodynamics aspects Thermodynamic parameters relevant to the sorption process are the change in standard Gibb's free energy (?G◦), entropy (?S◦) and enthalpy (?H◦); which can be determined using following equa- tions: ?G◦ = −RT ln KD (18) ln KD = − ?H◦ ?S◦ + RT R

15**(19) where R is the universal gas constant (8.314 J mol−1 K−1), T is the temperature (K) and KD is the** thermodynamic **distribution**

coeffi- cient, defined as: Ca KD = Ce (20) where Ca is the equilibrium metal concentration on the solid sur- face (mmol/L)

13**and Ce is the equilibrium** metal **concentration in the** bulk **solution** (mmol **/L). The** enthalpy **and** entropy change **can be calculated from the** slope **and** intercept **of** Van't **Hoff** plot **of ln** KD **vs 1/T** (Fig. 11). **The**

calculated thermodynamic parameters are given in Table 5. Negative values of ?G◦ are displayed in Table 5 at all temper- atures, which indicate the favorability and spontaneous nature of 3.0 2.8 2.6 2.4 2.2 ln KD 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.0030 0.0031 0.0032 0.0033 1/T (K-1) Fig. 11. Thermodynamic plot of ln KD versus 1/T of Ni-sorption onto cassava peel. Table 4 The fitted parameters of kinetic models for Ni-sorption onto cassava peel. Particle size (?m) qe exp (mmol/g) Kinetic model Pseudo-first order Pseudo-second order k1 qe R2 k2 qe R2 125–177 1.2304 0.0920 177–250 0.9933 0.0665 250–500 0.7418 0.0524 1.1840 0.9629 0.9787 0.9909 0.7297 0.9858 0.1039 1.2351 0.0772 1.0147 0.0754 0.7475 0.9903 0.9926 0.9936 Table 5 Thermodynamic parameters of Ni-sorption onto cassava peel. T (K) ?G◦ (kJ/mol) ?H◦ (kJ/mol) ?S◦ (kJ/mol K) R2 303.15 318.15 333.15 −2.738 46.584 0.162 0.9992 −5.077 −7.623 Ni-sorption process. As the temperature increases, the ?G◦ value becomes more negative which implies that higher temperature favors Ni-sorption. The positive value of ?H◦ denotes the endother- mic nature of this sorption process and acts as another evidence of its chemisorption nature since ?H◦ value lies between 20.9 and 418.4 kJ/mol [20]. This observation is also supported by the increased amount of adsorbed nickel at higher temperature. On the other hand, the positive value of ?S◦ denotes the internal structural changes of the cassava peel

38**due to the** intercalation **of Ni(II) ions** and **the** increase in **the**

disorder degree at solid–solution interface due to the desolvation in bulk solution during metal sorption process [21]. 4. Conclusions This work evaluates various aspects of Ni-sorption onto cassava peel waste.

Characterizations of adsorbent are conducted to ana- lyze the surface morphology and surface chemistry of cassava peel before and after metal sorption. To assess the feasibility of cassava peel waste to remove Ni(II) ions, the biosorption experiments are carried out in batch mode. The maximum uptake capacity (qm) of cassava peel is 57 mg/g at pH 4.5. The Sips model provides the best representation for adsorption equilibrium data. In kinetic data cor- relation, the

34**pseudo-second order is superior to** the **pseudo-first order model.**

The Ni-sorption mechanism is also discussed from molecular point of view. Lastly, thermodynamic results indicate the endothermic (?H◦ > 0), spontaneous (?G◦ < 0) and irreversible (?S◦ > 0) natures of Ni-sorption onto cassava peel. References

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