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1**Neem leaf utilization for copper ions removal from aqueous solution**

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4**Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia** b Division **of Chemical Engineering, The University of Queensland, St. Lucia, Qld 4072, Brisbane,**

15Adsorption of copper onto neem leaf powder was studied in batch

and continuous mode.

8Langmuir and Freundlich models were used to fit the equilibria data of which Langmuir model is

considered better in correlation. The maximum adsorption capacity of neem leaf powder was 18.29 mg/g (0.288 mmol/g). Column adsorption study to obtain the breakthrough curves was also presented on which Thomas model were chosen to represent the dynamic sorption data. Thermodynamics data indicated that the adsorption process is spontaneous, irreversible and endothermic. ß 2009 Taiwan Institute of

5Chemical Engineers. Published by Elsevier B.V. All rights reserved. 1. Introduction Water pollution normally occurs by direct discharge of

waste material or wastewater to surface water. Most significant problem in water pollution is largely caused by heavy metals. Heavy metal pollution originates from industrial wastewater namely electro- plating,

12metal finishing, metallurgical, tannery, chemical manu- facturing, mining and battery manufacturing industries

(Aksu and Donmez, 2006; Al-Rub, 2006; Kang et al., 2007). Heavy metals' traces in industrial wastewater brings a potential problem onto human health, thus, their removal from wastewater is of particular importance. A number of techniques are currently available to sequester heavy metals from industrial wastewater and adsorption onto activated carbon has become a quite common technique to treat industrial effluent containing heavy metals. Due to its uneconomic price, studies on alternative adsorbents have been intensified which focused mainly on biomass-based materials (Bhattacharyya and Sharma, 2004; Mungasavalli et al., 2007). Numerous studies already utilized neem leaves as alternative sorbent to remove heavy metal such as Pb (Bhattacharyya and Sharma, 2004) and Cd (Sharma and Bhattacharyya, 2005). Copper is a heavy metal widely found in polluted water canal systems in some parts of East Java (Indonesia), mostly comes from incomplete wastewater treatment. In this paper, neem leaf's performance to adsorb Cu from aqueous solution is probed.

6Surface structures of neem leaf remains stable during long time agitation treatment,

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highlighting its advantage as adsorbents (Bhattacharyya and

Sharma, 2004). 2. Materials and methods 2.1. Materials Cupric sulfate hexahydrate, CuSO4 6H2O (analytical grade) was

> 14**purchased from Sigma–Aldrich** (Singapore) **and used as** heavy metal model **without** any **further**

treatment. Dried neem leaves collected from Probolinggo (East Java, Indonesia) were pulverized onto fine powder by grinding inside a mechanical grinder. The pHpzc of the neem leaf was determined from acid-based titration (Wibowo et al., 2007). 2.2.

> 11**Characterization of the** neem leaf **Characterization of biosorbent'** s **surface and structure hold keys to understanding the metal binding mechanism onto biomass.**

Fourier transform infra-red (FTIR), energy-dispersive X-ray spectroscopy and X-ray mapping were used here.

> 8**FTIR spectroscopy** technique **was used to** determine **the functional groups** available **in**

neem leaf. FTIR spectrometer (Shimadzu 8400s) equipped with KBr window were used to analyze neem leaf powder (wavenumber range: 400–4000 cm 1). SEM were per- formed using JEOL JSM-6400F field emission SEM. The observation of samples was conducted at an accelerating voltage of 10 kV, aperture of 4, 37 mm working distance, and spot size of 8. Energy- dispersive X-ray and X-ray elemental mapping analysis was

> 13**performed on JEOL JSM-6460 LA low vacuum analytical SEM equipped with an integrated JEOL Hyper mini-cup,**

133 eV

> 2**1876-1070/$ – see front matter ß** 2009 **Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved. doi:10.1016/j.jtice.** 2009 **.04.**

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resolution, SiLi crystal, ultra thin window (UTW) and energy- dispersive X-ray spectrometer. 2.3. Batch and continuous adsorption experiments The pH effect was studied at pH range of 2.0–6.0 since metal precipitation onto its hydroxide takes place at pH above 6.0.

17**To adjust the pH, appropriate amount of**

H2SO4 solution was added to the solution. Batch adsorption experiments were conducted by shaking the Erlenmeyer flasks filled with a mixture of neem leaf powder and copper solution for predetermined period at 30, 50 and 70 8C in a shaker bath MEMMERT SV-1422. Adsorption isotherm study was carried out with

15**initial Cu(II) concentration of** 200 mg **/L.** The initial **pH** value **of 5.0**

(optimum pH) was used for all experiments. The adsorbent dosage is maintained between 0.5 and 2.2 g. Cu(II) solution was prepared by diluting 0.781 g of CuSO4 5H2O in 1000 mL distilled water, of which only 50 mL is used each time. The solution concentration was analyzed by UV– Vis Genesys 10 v spectrophotometer at 352 nm. Continuous adsorption experiments were conducted as follow: neem leaf powder was packed

7**in a glass column with** a **diameter of 1.** 7 **cm and a** height **of** 10 **cm.** Cu(II) solutions **was**

7**pumped through the column by peristaltic pump (Masterflex**

7550-62). This experiment was performed to obtain breakthrough curves at different flow rates (8.5 and 9.4 mL/min), feed concentrations (400, 500 and 600 ppm) and bed height (4, 5 and 6 cm). Solutions were collected at the column outlet after each fixed time intervals and analyzed for its copper concentration. 3. Results and discussion 3.1. Characteristic of neem leaf before and after adsorption

9**Functional groups on neem leaf powder were analyzed using FTIR. Diverse type of functional groups are available, namely** C **–H bending**

(985.56–1472.55 cm 1), C–H stretching (2845.77– Fig. 1. Fourier transform infra-red (FTIR) spectra of neem leaf powder before and after adsorption. 2909.42 cm 1), O–CH3 (1475.12 cm 1), C 5C, ketone (1575.73–1748.35 cm 1), carboxylic (1319.22–1717.49 cm 1), amides (1575.73 cm 1), aromatic (754.12–762.79 cm 1), C–O–C stretch- ing (1164.92 cm 1), sulfur compounds (1097.42–1339.47 cm 1), alcohols and phenols (1271–3627.85 cm 1). FTIR spectra are depicted in Fig. 1. After sorption, several functional groups which were initially present disappear, while some other had their position altered. For example, on alcohols and phenols group, O–H bending was not detected after Cu(II) sorption, while peaks Fig. 2. (a) SEM and EDX spectra of Cu loaded neem leaf powder, (b) SEM and X-ray elemental mapping for Cu on Cu-loaded neem leaf powder. N. Febriana et al. /

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113 Fig. 3. Effect of solution pH on the sorption of Cu(II) on neem leaf (Co = 200 mg/L, and mass of neem leaf 0.5 g). characteristics of O–H bending and C–O stretching (chelating compounds) shifted from 2894.95 to 2882.42 cm 1. Same ten- dency were observed for carboxylic groups. Yet, several char- acteristic bonding such as C–H stretching and S 5O stretching are not influenced by the adsorption process. Fig. 2(a) shows

the SEM-EDX results for neem leaf after copper ion adsorption, on which copper's existence on the surface is confirmed from Cu K and L peaks. SEM and Cu elemental mapping on a particular surface spot after adsorption is also given in Fig. 2(b). Bright spots indicate copper's presence, of which the copper's distribution was not uniform. This would mean that only some functional groups on the surface were responsible for the copper uptake from the solution. 3.2. Adsorption studies The pHpzc of neem leaf is 4.5. Cu(II) uptake was affected by pH in the range of 2.0–6.0 as indicated in Fig. 3. At low pH the amount of Cu(II) uptake was also low and enhanced with increasing pH from 2.0 to 5.0. The highest percentage removal of Cu(II) on neem leaf were observed between the pH 4.0 and 6.0. At pH < pHpzc, the acidic water donates more protons than hydroxide groups and the surface charge of neem leaf is positive, causing the protons presents in the solution to compete strongly with Cu(II) ions for the active sites

> 16**on the surface of** neem leaf, **resulting in** lower amount **of** Cu **(II)**

uptake. With pH rise, electrostatic repulsion between Cu(II) and surface sites as well as the competing effect of protons decreased which proves to be more beneficial toward Cu(II) ions uptake. To correlate the adsorption equilibria data, Langmuir and Freundlich models are employed. Langmuir model has the form of qe ¼ qmax 1 þKLKCLeCe (1) and Freundlich has the form of qe ¼ K f Ce1=n (2)

> 3**where qe is the amount adsorbed at equilibrium** condition, **qmax is the Langmuir constant which is equal to adsorption capacity. KL represents Langmuir sorption equilibrium constant** while **Ce is equilibrium concentration.**

KF and n on the other hand are Freundlich constants.

> 12**Langmuir and Freundlich** fitting **plots are** shown **in** Fig. **4(** a). Its parameters **and**

correlation coefficient values (R2) are summarized Fig. 4. (a) Biosorption isotherms of copper on neem leaf powder, (b) effect of bed height on the breakthrough curve, (c) effect of concentration on the breakthrough curve. in Table 1. It is obvious that Langmuir equation fits the data better that Freundlich equation, which is also evidenced by better correlation coefficient value in Table 1.

> 14**Freundlich equation fails to** predict **the adsorption** experimental **data at**

high equilibrium concentration due to the inavailability of saturation capacity term in its equation. While qmax (maximum adsorption capacity) increased from 2.85 10 4 to 2.88 10 4 mol/g, KL (Langmuir equilibrium constant) was enhanced from 2567 to 5223 (L/mol) along with temperature rose. The enhancement of maximum adsorption capacity (qmax) as a function of temperature is a strong indication that the chemisorption is the control mechanism. One of the distinct features of the chemisorption is the increase of 114 N. Febriana et al. /

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Table 1 Isotherm constants of Freundlich and Langmuir models for sorption process. Heavy metal ion Temperature (8C) Freundlich Langmuir KF (mg/g) N R2 Qmax (mol/g) 104 KL (L/mol) R2 Cu2+ 30 1.78 50 2.24 70 2.78 1.99 0.975 2.16 0.961 2.35 0.978 2.84 2567 2.86 3545 2.88 5223 0.991 0.995 0.997 adsorption capacity with temperature. Another indication is the high value of KL. The KL value can be correlated with adsorption enthalpy change (DH8). Due to the endothermic nature of chemisorption, DH8 value would be positive. Therefore, in parallel to temperature increase, KL value should also rise. Fig. 4(b) shows the breakthrough curve for a fixed initial concentration of 500

5**mg/L** and **flow rate** 8.5 **mL/min** with different **bed height**

of 4, 5 and 6 cm. Fig. 4(c), on the other hand displays the breakthrough curve for fixed bed height of 5 cm and flow rate 8.5 mL/min with different initial copper concentration of 400, 500 and 600 mg/L. The dynamic column data were fitted by Thomas model to determine the equilibrium specific uptake of copper (q0) and also its rate constant (KTH). Thomas model (Thomas, 1944) is defined as Ct 1 Co 1 þ exp½KTHðqem CoVe f f =vÞŠ ¼ (3) where KTH is Thomas rate constant, while Ct and Co are the concentration of metal in the effluent and influent, respectively. In addition,

18**Veff is the volume of effluent and m is the mass of** biosorbent **in the column.**

Bed height effect on the breakthrough curves can be clearly seen in Fig. 4(b). The breakthrough time increase as the bed height increases. Furthermore, the amount of cooper ions adsorbed also increases for larger bed height. Accordingly, at larger bed height, the distance for mass transfer zone is longer, resulting in higher value of breakthrough time which is mainly caused by the higher contact time between metal ions solution and neem leaves powder surface. The effect of influent concentrations on the breakthrough curves is also shown in Fig. 4(c). Increasing the influent concentration enhances the total adsorption capacity, hence the breakthrough curve become steeper as the feed concentration increase. 3.3. Thermodynamic of adsorption

3**Free energy change** (DG8) **is a fundamental criterion of process spontaneity** which **can be estimated**

from DG ¼ RT ln KL (4) where KL is equilibrium constant obtained from Langmuir model (L

10**/mol), T is the absolute temperature (K) and R is the gas constant (8.314 J/mol K). The**

correlation between free energy change, enthalpy change (DH8) and entropy change (DS8) is given by DG ¼DH TDS (5) The values of DG8 obtained at 30, 50 and 70 8C are -19.78, 21.96, and 24.42 kJ/mol, respectively.

16**Negative values of** DG8 denotes **the** spontaneity **nature of the adsorption**

(Ho and Ofomaja, 2006). A positive DH8 value (15.43 kJ/mol) indicates that the process is endothermic as well as suggesting the high probability for chemisorption as the controlling mechanism. Additionally, posi-

tive value of DS8 (0.116 kJ/mol K) indicates that the process is irreversible which again is the characteristic of chemisorption (Aksu and Tunc, 2005). 4. Conclusion This study probes the performance of neem leaf biomass waste to sequester copper from aqueous solution.

> 6**Neem leaf serves as a** potential **alternative adsorbent to remove** copper **ions from** copper containing **solution.**

The

> 17**adsorption experiments were conducted in batch** and dynamic modes **at** optimum **pH**

of 5. Adsorption equilibria data were also fitted by the well-known adsorption models, Freundlich and Langmuir. Langmuir equation represents the adsorption equilibria better than Freundlich. Thermodynamics data indicated that the adsorption of copper ion onto neem leaf is endothermic. Chemisorption can be pointed out as the controlling mechanism. Carboxylic groups, alcohols and phenols were involved in the binding process. Lastly, the dynamic data was also provided in the form of breakthrough curve along with Thomas model representation. Acknowledgements The authors would like to thank A/Prof. João C. Diniz da Costa from FIMLab, Division of Chemical Engineering, the University of Queensland, Australia for his support in terms of SEM equipment access. References Aksu, Z. and O. Tunc, "Application of Biosorption for Penicillin G Removal: Comparison with Activated Carbon," Process Biochem., 40, 831 (2005). Aksu, Z. and G. Donmez, "Binary Biosorption of Cadmium(II) and Nickel(II) onto Dried Chlorella vulgaris: Co-Ion Effect on Mono-Component Isotherm Parameters," Process Biochem., 41, 860 (2006). Al-Rub, F. A. A., "Biosorption of Zinc on Palm Tree Leaves: Equilibrium, Kinetics, and Thermodynamics Studies," Sep. Sci. Technol., 41, 3499 (2006). Bhattacharyya, K. G. and A. Sharma, "Adsorption of Pb(II) from Aqueous Solution by Azadirachta indica (Neem) Leaf Powder," J. Hazard. Mater., B113, 97 (2004). Ho, Y. S. and A. E. Ofomaja, "Biosorption Thermodynamics of Cadmium on Coconut Copra meal as Biosorbent," Biochem. Eng. J., 30, 117 (2006). Kang, S., J. Lee, and K. Kima, "Biosorption of Cr(III) and Cr(VI) onto the Cell Surface of Pseudomonas aeruginosa," Biochem. Eng. J., 36, 54 (2007). Mungasavalli, D. P., T. Viraraghavan, and Y. C. Jin, "Biosorption of Chromium from Aqueous Solutions by Pretreated Aspergillus niger: Batch and Column Studies," Colloids Surf. A: Physicochem. Eng. Aspects, 301, 214 (2007). Sharma, A. and K. G. Bhattacharyya, "Azadirachta indica (Neem) Leaf Powder as a Biosorbent for Removal of Cd(II) from Aqueous Medium," J. Hazard. Mater., B125, 102 (2005). Thomas, H. C., "Heterogeneous Ion Exchange in a Flowing System," J. Am. Chem. Soc., 66, 1664 (1944). Wibowo, N., L. Setyadhi, D. Wibowo, and J. Setiawan, "Adsorption Benzene and Toluene from Aqueous Solutions onto Activated Carbon and Its Acid and Heat Treated Forms: Influence of Surface Chemistry on Adsorption," J. Hazard. Mater., 146, 237 (2007).