# Turnitin Originality Report

CEJ-10211 by Suryadi Ismadji

From journal (Hippo-hippo)

Processed on 15-Feb-2018 21:58 WIB
ID: 916441500
Word Count: 10760

| Similarity Index | Similarity by Source | |
|---|---|---|
| 16% | Internet Sources: | 10% |
| | Publications: | 11% |
| | Student Papers: | 4% |

## sources:

**1** 2% match (Internet from 06-Nov-2014)
http://widyamandala.academia.edu/SuryadiIsmadji/Papers

**2** 1% match (student papers from 06-Nov-2016)
Submitted to University of Oklahoma on 2016-11-06

**3** 1% match (Internet from 31-Oct-2017)
https://collections.plymouth.ac.uk/bitstream/handle/10026.1/4189/2015haswell301281491DSc.pdf?isAllowed=y&sequence=1

**4** 1% match (publications)
Hokkanen, Sanna, Amit Bhatnagar, Eveliina Repo, Song Lou, and Mika Sillanpää. "Calcium hydroxyapatite microfibrillated cellulose composite as a potential adsorbent for the removal of Cr(VI) from aqueous solution", Chemical Engineering Journal, 2016.

**5** 1% match (publications)
Ismadji, Suryadi, Felycia Edi Soetaredjo, and Aning Ayucitra. "The Equilibrium Studies in the Adsorption of Hazardous Substances Using Clay Minerals", SpringerBriefs in Molecular Science, 2015.

**6** 1% match (publications)
Ong, L.K., A. Kurniawan, A.C. Suwandi, C.X. Lin, X.S. Zhao, and S. Ismadji. "A facile and green preparation of durian shell-derived carbon electrodes for electrochemical double-layer capacitors", Progress in Natural Science Materials International, 2012.

**7** 1% match (Internet from 24-Jul-2015)
http://www.cugb.edu.cn/upload/20600/papers_upload/259.pdf

**8** 1% match (student papers from 26-Sep-2017)
Submitted to Universiti Malaysia Terengganu UMT on 2017-09-26

**9** 1% match (publications)

Kurniawan, A.. "Performance of durian shell waste as high capacity biosorbent for Cr(VI) removal from synthetic wastewater", Ecological Engineering, 201106

**10** < 1% match (publications)
Silke Schiewer, Bohumil Volesky. "Modeling Multi-Metal Ion Exchange in Biosorption", Environmental Science & Technology, 1996

**11** < 1% match (publications)
Papita Saha, Shamik Chowdhury. "Chapter 16 Insight Into Adsorption Thermodynamics", InTech, 2011

**12** < 1% match (publications)
Ong, L.K., A. Kurniawan, A.C. Suwandi, C.X. Lin, X.S. Zhao, and S. Ismadji. "Transesterification of leather tanning waste to biodiesel at supercritical condition: Kinetics and thermodynamics studies", The Journal of Supercritical Fluids, 2013.

**13** < 1% match (Internet from 23-May-2016)
http://dar.aucegypt.edu/bitstream/handle/10526/4549/Thesis%20Report_%20Hayam%20_Final.pdf?sequence=1

**14** < 1% match (publications)
Li, W. C., F. Y. Law, and Y. H. M. Chan. "Biosorption studies on copper (II) and cadmium (II) using pretreated rice straw and rice husk", Environmental Science and Pollution Research, 2015.

**15** < 1% match (publications)
Moghaddam, Mohammad Ramezani, Shohreh Fatemi, and Alireza Keshtkar. "Adsorption of lead (Pb2+) and uranium cations by brown algae; experimental and thermodynamic modeling", Chemical Engineering Journal, 2013.

**16** < 1% match (Internet from 09-Feb-2015)
http://www.ijmer.com/papers/Vol3_Issue5/EA3532553266.pdf

**17** < 1% match (publications)
Soenjaya, Soegiarto Adi, Nova Handoyo, Felycia Edi Soetaredjo, Artik Elisa Angkawijaya, Yi-Hsu Ju, and Suryadi Ismadji. "Preparation of carbon fiber from water hyacinth liquid tar", International Journal of Industrial Chemistry, 2014.

**18** < 1% match (Internet from 27-Nov-2017)
http://awc.ksu.edu.sa/sites/awc.ksu.edu.sa/files/imce_images/04-adsorption_of_copper_cu2_from_aqueous_solution_using_date_palm_trunk_fibre_isotherms_and_kinetics.pdf

**19** < 1% match (publications)
Ahmad, A.. "Removal of Cu(II) and Pb(II) ions from aqueous solutions by adsorption on sawdust of Meranti wood", Desalination, 200910

**20** < 1% match (publications)
R. V. P. Ferreira, E. A. Silva, R. L. S. Canevesi, E. G. A. Ferreira et al. "Application of the coconut fiber in radioactive liquid waste treatment", International Journal of Environmental Science and Technology, 2017

**21** < 1% match (Internet from 28-Dec-2017)
https://www.scipedia.com/public/Luiza-Postai_et_al_2016a

**22** < 1% match (publications)
Pojananukij, N., K. Wantala, S. Neramittagapong, and A. Neramittagapong. "Equilibrium, kinetics, and mechanism of lead adsorption using zero-valent iron coated on diatomite", Desalination and Water Treatment, 2015.

**23** < 1% match (Internet from 01-Apr-2016)
http://tdx.cat/bitstream/handle/10803/284239/hz1de1.pdf?sequence=1

**24** < 1% match (publications)
Tan, I.A.W.. "Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon", Chemical Engineering Journal, 20070301

**25** < 1% match (publications)
Haider, S.. "Preparation of the electrospun chitosan nanofibers and their applications to the adsorption of Cu(II) and Pb(II) ions from an aqueous solution", Journal of Membrane Science, 20090220

**26** < 1% match (publications)
Imessaoudene, Djillali, Salah Hanini, Abdelkader Bouzidi, and Abderrahmane Ararem. "Kinetic and thermodynamic study of cobalt adsorption by spent coffee", Desalination and Water Treatment, 2015.

**27** < 1% match (Internet from 28-Mar-2014)
http://www.lume.ufrgs.br/bitstream/handle/10183/63143/000869354.pdf?sequence=1

**28** < 1% match (Internet from 14-Oct-2014)
http://cdn.intechopen.com/pdfs-wm/21870.pdf

**29** < 1% match (Internet from 08-Jul-2015)
http://www.asocse.org/journals/NP/PDF/20150101SI.pdf

**30** < 1% match (publications)
Chiban, M.. "Single, binary and multi-component adsorption of some anions and heavy metals on environmentally friendly Carpobrotus edulis plant", Colloids and Surfaces B: Biointerfaces, 20110201

31 < 1% match (Internet from 05-May-2016)
http://ijens.org/Vol_15_I_02/158402-7676-IJET-IJENS.pdf

32 < 1% match (Internet from 19-Sep-2010)
http://faculty.qu.edu.qa/almuhtaseb/CV/Papers/Ads%20of%20Al.pdf

33 < 1% match (Internet from 30-Oct-2013)
http://www.tdx.cat/bitstream/handle/10803/7802/tceo.pdf.txt?sequence=8

34 < 1% match (publications)
Hb25_Springer Handbook of Marine Biotechnology, 2015.

35 < 1% match (publications)
Gunay, A.. "Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics", Journal of Hazardous Materials, 20070719

36 < 1% match (publications)
Gyliene, O.. "Removal of free and complexed heavy-metal ions by sorbents produced from fly (Musca domestica) larva shells", Water Research, 200209

37 < 1% match (student papers from 06-Oct-2017)
Submitted to Our Lady of Fatima University on 2017-10-06

**paper text:**

Chemical Engineering **Journal**

7219 (2013) 137–148 Contents lists available at SciVerse ScienceDirect Chemical Engineering Journal journal homepage: www.elsevier.com/locate/cej

10Incorporation of selectivity factor in modeling binary component adsorption isotherms for heavy metals-biomass system Felycia Edi Soetaredjo ⇑, Alfin Kurniawan, Ong Lu Ki, Suryadi Ismadji Department of Chemical Engineering,

Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia highlights " Utilisation of rice straw as a cheap and effective sorbent for the removal of Cu and Pb ions. "

1Incorporation of selectivity factor of solute for the modification of extended-Langmuir model." Representation of binary adsorption data and the model fittings in 3D plots. "Application of biosorption study using real effluent from a wastewater treatment plant. " Regeneration study of biosorbent for industrial practice. article info

7Article history: Received 21 October 2012 Received in revised form 19 December 2012 Accepted 26 December 2012 Available online 11 January 2013 Keywords:

Biosorption Rice straw Extended Langmuir Selectivity Binary components abstract The

1single and binary biosorption of copper and lead ions from aqueous solution using a low cost agro- based resource (i.e. rice straw) has been demonstrated in this work. The biosorption experiments were performed in a static mode. Experimental parameters affecting the sorption process namely biosorbent dose, pH, and temperature were studied. Two empirical adsorption models (i.e. Langmuir and Freundlich) were used for the evaluation of biosorption equilibrium data in single system. Both models were able to correlate experimental data satisfactorily. The adsorptivity of solute (KL) and maximum sorption capacity of the solid (qm) were increased at higher temperatures. For binary metal system, we modified the adsorption parameters of extended-Langmuir model (i.e. KL-bin and qm-bin) by

**introducing selectivity** fac- tor **of the solute (S). It was found that the modified extended-Langmuir model with incorporation of** sol- ute’s **selectivity factor gave good correlation results against binary adsorption data with reasonable fitted parameter values. The feasibility and biosorption performance of rice straw in sequestering copper and lead ions was also tested using real effluent along with its regeneration possibility.**

Ó 2013 Elsevier B.V. All rights reserved. 1. Introduction Heavy metals are a type of pollutants that

37**are generated from various industrial activities such as metal plating, mining,** metal- lurgical, **leather tanning, batteries,** alloy, **and electronic**

goods man- ufacturing. Despite of their importance for economic growth in most countries including Indonesia, the discharged wastewater containing considerable amounts of heavy metal ions is of a major concern to the environment. The contamination of

8**heavy metals in the surface waters, groundwater, and soil causes deterioration of soil and water qualities and gives adverse impacts on the growth of terrestrial and aquatic organisms**

[1–3]. Moreover, the distribu- tion and accumulation of this substance in food chains often pose serious threats to public health [4,5]. Copper (Cu) and lead (Pb) are two kinds of heavy metals that are widely used since ancient times ⇑

6**Corresponding author. Tel.: +62 31 389 1264; fax: +62 31 389 1267.**

E-mail address: felyciae@yahoo.com (F.E. Soetaredjo).

7**1385-8947/$ - see front matter Ó 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.cej.2012.12.**

077 and their negative effects on human health have been assessed [6]. The Indonesian government has set the regulation for maximum levels of Pb and Cu ions in industrial effluents discharged into in- land surface waters (Table 1). To obey this regulation, the indus- tries have to treat their effluents properly before discharge into environment. Many conventional methods are available for the treatment of metal-bearing effluent such as electrochemical [7], biological treat- ment [8], membrane separation [9], coagulation [10], chemical pre- cipitation [11], reverse osmosis [12], solvent extraction [13], and ion exchange [14]. However, the application of such methods is of- ten limited,

8**particularly in handling effluents containing trace amounts of heavy metal ions (1–100 mg/l) due to** incomplete **metal removal, energy-intensive,** economically **expensive, and**

generation of secondary waste products (e.g.

8**toxic sludge) that require proper disposal techniques without** creating any problem **to the**

environ- ment. To this end, adsorption has proven as a cost-effective and high efficiency method that produced high quality effluents with Table 1 The maximum levels of lead and copper heavy metals in industrial effluents discharged into inland surface waters. Category Target of uses Leada Coppera A Drinking water (direct-consumed) B Bottled drinking water C Fishery and livestock D Agricultural, urban business, industry, and hydro power-plant 0.05 1 0.1 1 0.03 0.02 1 0.2 a In the unit concentration of mg/l. minimum environmental impacts [15]. One of the key successes of adsorption process in removing heavy metal ions from water and wastewater lies in the selection of the adsorbing material (or adsor- bent). To ensure the effectiveness and economic feasibility of the process, the adsorbents should have the following criteria: (1) high loading capacity; (2) cheap; (3) abundant availability; and (4) regenerable. Out of criteria above, commercial activated carbons may satisfy the first and the fourth criteria while the second and the third become the main limitations for large-scale use of this adsorbent in water and wastewater treatment processes. Recently, the lignocellulosic solid wastes generated from agri- cultural and forestry sectors have been highlighted as potential adsorbents for the removal of heavy metal ions from water and wastewater [16]. Among the aforesaid criteria, the lignocellu- losic-based adsorbents may satisfy three or all criteria although their adsorption capacities are lower than activated carbons. Rice straw that produced from harvesting process of paddy can be uti- lised as a low cost and effective biosorbent for such purpose. This crop waste mainly composed of natural polymer materials such as lignin, cellulose, and hemicelluloses, which are known to be the binding sites of heavy metal ions [16]. The availability of rice straw in Indonesia is huge with total production reached eighty millions tons in 2011. Of this amount, 30–40% have been used as cattle feeds, 7–15% have been used for handicrafts making, and the rest (about 50%) ends up as a waste [17]. A common method to reduce excess quantities of rice straw is by incineration, which not only causes an air pollution but also waste of natural resources. Therefore, an advantageous waste management process for unused rice straw is by utilising them as a biosorbent for purifying metal- bearing effluents. This work deals with the evaluation of biosorption performance of rice straw

30**for the removal of** copper **and** lead ions **in single and binary component systems.**

Although

34**biosorption studies of heavy metal ions** in single system using pristine or chemically-modified rice straw have been well reported in the last few years [18–21],

20**however, the adsorption equilibria aspect of multicomponent** sys- tem **and its modeling still needs to be explored.**

Several adsorption models such as extended-Langmuir, extended-Freundlich, and ideal adsorption solution theory (IAST) models (e.g. Fast-IAS the- ory, real adsorption solution theory) have been developed to de- scribe multicomponent adsorption equilibria. Despite of their reasonable success, the applications of IAST and its modified forms are restricted due to their complex algorithm and the use of an elaborate computer programming for solving the model. In other hand, extended-Langmuir

20**is the most extensively used** model fea- turing **its simple approach in describing multicomponent**

adsorp- tion equilibria. The correlation of adsorption equilibrium data by extended-Langmuir model is mostly performed through a compar- ison between experimental and theoretical amounts of qe (i.e. the equilibrium concentration of adsorptive in the adsorbed state). However, this procedure lacks of theoretical sounds and often fails to describe experimental data satisfactorily because it does not ad- dress the competitive adsorption in the system. To respond this problem, we propose modification on the adsorption parameters of extended-Langmuir model that incorporates selectivity factor of the solute (S). To the best of our knowledge, there is no report in the literature regarding the incorporation of solute's selectivity factor for the modification of extended Langmuir parameters (i.e. qm-bin and KL-bin) and its model fitting against binary adsorption equilibrium data of heavy metals-biomass system. The regenera- tion and metal recovery studies of spent biosorbent were also con- ducted in order to evaluate the feasibility and reliability of rice straw for practical applications. 2. Experimental sections 2.1. Chemicals Analytical grade CuSO4 5H2O and Pb(NO3)2 as metal ion sources were purchased from Sigma–Aldrich, Singapore. Deionized water was used throughout all experiments in this work. 2.2. Preparation of biosorbent Rice straw

12**in this work was collected from a** rice field **located**

near the border of Lumajang city,

6**East Java, Indonesia. After the collection, the** straw **was cut into a size of 1**

1 cm and boiled with deionized water for 2 h to remove color materials. The decolorized straw was then

29**washed with deionized water three times and dried in an oven at 80 °C for 24 h. The** biomass was then

6**crushed with an IKA-Labortechnick grinder** and sieved **to obtain particle size of**

150–180 lm. Finally, the product was kept in airtight plastic bag for further experimental use. 2.3. Characterizations of biosorbent The surface morphology of rice straw was visualized in a JEOL JSM-6300F

17**field emission scanning electron microscopy. Prior to** scanning, **the** sample was **coated with a** conductive film **of**

plati- num

17**using an Eiko IB-5 sputter-coater operated at 6 mA for** 4 **min in argon atmosphere. The**

surface scanning was performed at an electron acceleration voltage of 20 kV, four aperture, eight spot size, and 9 mm working distance. The pore structure of rice straw was analyzed by a Quadrasorb SI sorption analyzer using nitrogen as the adsorbate at 77.15 K and relative pressure (p/p0) ranging from 0.005 to 0.995. The specific surface area of biosorbent was obtained by means of the BET meth- od applied at p/p0 range of 0.06–0.3. The

9**surface functional groups of biosorbent were** identified by **infrared spectroscopy**

technique, using

6**a Shimadzu FTIR-8400S spectrophotometer. The**

analysis was conducted

6**based on the KBr disk** method **with** 200 **cumulative scans**

in a scanning range of 4000–500

22**cm 1. The** pH **of** point of **zero charge (pHpzc)** of rice straw **was** deter- mined by pH-drift method [22] and found to be 3.2. Han and Rowell method [23] was applied for quantification of the percentage composition of lignin, cellulose, and hemicellulose in rice straw (wt%, dry matter) and it was found to be 17.4%, 38.2%, and 20.6%, respectively. The composition of inorganic matters (minerals) in rice straw such as Na, K, Mg, and Ca was analyzed by a MiniPal QC energy dis- persive X-ray fluorescence spectrometer (PANalytical) and the re- sults are given as follows:

13**Na = 0.09%; K = 1.87%; Mg = 0.23%; and Ca = 0.52%.**

2.4. Static biosorption experiments The stock solutions of copper and lead ions at initial concentra- tion of 100

36**mg/l (1.** 57 **mmol/l – Cu(II) and**

0.48 mmol/l – Pb(II)) were prepared by dissolving a known amount of CuSO4 5H2O and Pb(NO3)2 into 500 ml deionized water. The single and binary bio- sorption isotherm experiments were performed by adding a pre- scribed amount of biosorbent ranging from 1 g to 20 g

9**into a series of** stoppered **conical flasks containing** 100 ml **metal solution. The flasks were** then **placed in a** Memmert **thermostatic** shaker **water-bath**

and shaken at desired temperature (30 °C, 40 °C, 50 °C, and 60 °C) with a shaking speed of 100 rpm. Preliminary experiments show that biosorption equilibrium time was reached within 3–4 h. Subsequently, the flasks were removed from the bath and the mixture was filtered pass through a Whatman filter paper to remove solid particles. The residual concentration of metal ions in the filtrate was analyzed using a Shimadzu AA-6200 atomic absorption flame emission spectrophotometer. The measurements were performed at a wavelength corresponding to the maximum absorbance of each metal ion species, i.e. 324.4 nm for copper and 216.7 nm for lead. The

19**effect of pH on the** biosorption **of Cu(II) and Pb(II) ions**

30**in single and binary component systems was**

investigated at

18**pH range of 1–6** since **the** formation **of** metal hydroxide precipitates, **i.e.**

Cu(OH)2 and Pb(OH)2, occurs at pH higher than 6. The pH of metal solutions was adjusted by the addition of 0.1 M HCl solution as per required. 2.5. Calculations The amounts

14**of Cu(II) and** Pb **(II) ions** adsorbed **onto rice straw in**

single solute system were calculated by following equation: ðC0 CeÞ qe ¼ m V ð1Þ

21**where C0 and Ce are the initial and equilibrium concentrations** of metal ions **in the liquid phase** (mmol/l), **V is the volume of** metal **solution** (l), qe **is the amount of**

metal ions adsorbed per unit of bio- sorbent mass (mmol/g), and m is the mass of biosorbent (g). The equilibrium concentration of metal i species (Ce,i) in binary mixture can be calculated by the same manner using following mass balance equation: qe;i ¼ ðC 0;i Ce;iÞ m V ð2Þ where qe,i

15**is the** equilibrium **amount of** solute i **in** the **adsorbed phase (mmol/g),**

C0,i and Ce,i are the initial and equilibrium concen- trations of solute i in the liquid phase (mmol/l), respectively. For reproducibility test, all experiments were repeated three times with averages used as the results. 3. Results and discussion 3.1. Characterizations of biosorbent The surface morphology of rice straw, as visualized by SEM at magnifications of 5000 and 10000 is depicted in Fig. 1. It was found that rice straw belongs to a nonporous solid material with respect to its surface smoothness. This surface characteristic was also revealed from the N2 adsorption–desorption isotherm results (figure not shown). The specific surface area of rice straw (SBET) is fairly low (40.7

24**m2/g) with total pore volume** (VT) **of 0.** 11 **cm3/g**

at STP. Low N2 sorption capacity of rice straw may be ascribed to the low porosity in the solid matrices. The presence of natural heteropolymer materials like lignin, cel- lulose, and hemicelluloses in biosorbent was evidenced from FTIR results (spectra not shown). Several strong absorption bands were noted at wavenumbers of 3618 cm 1, 2941 cm 1, and 1127 cm 1.

6**These bands correspond to** the OAH **stretch of** phenol **groups,** CAH **stretch of** alkanes **groups, and** CAO **stretch of**

13**carboxylic acids,** alkoxy **groups, or fiber carbonaceous that** presented **in the** ligno- cellulosic **structure.** The presence **of**

aromatic CAC stretch and ali- phatic C@C stretch was observed at wavenumbers of 1596 cm 1 and 1671 cm 1, respectively. Two moderate bands at wavenum- bers of 1082 cm 1 and 464 cm 1 reflected the vibration of silica- eous groups, associated with SiAO stretch and SiAO bend, respectively. After biosorption, several absorption bands namely OAH stretch and CAO stretch were altered. The reduced peak energy and the shifting of OAH stretch from 3618 cm 1 to 3583 cm 1 were due to the deformation of this band after metal ions binding. Another shifting was observed in CAO stretch from 1127

23**cm 1 to** 1079 **cm 1 and** SiAO stretch **from** 1082 **cm 1 to** 1051 **cm 1,** indi- cating **the**

involvement of these functional groups in the metal sorption process. Moreover, two new peaks at around 1400 cm 1 and 1600 cm 1 were observed, associated with the vibration bands of metal-carboxylate functional groups (COO-M) where M refers to lead or copper ions. This result implies that the binding of metal ions onto rice straw takes place via complexation or chelating mechanism with hydroxylate and carboxylate surface groups as the main adsorption sites and silicaeous groups in lesser extent through unidentate or bidentate coordination types. In order to investigate whether

10**ion exchange plays a major role in the metal**

sorption process, the concentrations of inorganic mat- ters such as Na, K, Ca, and Mg in the solid before and after biosorp- tion were analyzed. It was found that the concentrations of these minerals in pristine and metal-loaded biosorbents were slightly different and can be regarded essentially unchanged. This denotes that the binding of metal ions onto rice straw predominantly oc- curred by surface complexation or chelation mechanism (as evi- denced from FTIR results) and ion exchange in lesser extent. For the latter mechanism, it was found to be predominant in the bio- sorption using algae or seaweed biomass, as verified in several studies [24–26]. 3.2. Effects of pH The adsorption behavior of heavy metal ions and other contam- inants such as dyes, natural organic matters, etc. in aqueous phase strongly depends on pH and may be different for each solute-sor- bent interaction. The pH-dependence of metal biosorption has been verified by many researchers, which are relevant to the ionic state of surface functionalities on the adsorbent and the metal chemistry in the solution. The effect of pH on the removal of Cu(II) and Pb(II) ions by rice straw from single and binary mixture was investigated in a pH range of 1–6 and the results are shown in Fig. 2. It can be seen that the percentage removal of both metal ions steeply increased with increasing pH from 3 to 5, continued by a slight increase with increasing pH from 5 to 6. For binary compo- nent system, the highest percentage removal of metal ions was ob- served at pH about 6. Hence, pH 6 was selected as the optimum point and used throughout single and binary biosorption experi- ments in this work. At pH value below the pHpzc of biosorbent (i.e. pH 1–3), the sur- face functional groups on the solid (primarily carboxylic acids) were protonated by hydronium ions (H+) hence the

16**overall surface charge on the** solid was **positive. The** protonation **of**

carboxylic acid surface groups by H+ ions occurred as follows: R-COOH þ Hþ ! R-COOHþ2 ð3Þ As the result, an electrostatic repulsion force was generated be- tween metal ions and positively charged solid surface that retards metal binding process. In addition, high concentrations of H+ ions in the solution also competed with metal

5**species for the adsorption sites on the solid surface.**

Fig. 1. SEM micrographs of rice straw at magnifications of 200 and 1000 . 100 80 l v 60 a o m e R % 40

33**20 0 Cu(II) + Pb(II)** 6.08 **Pb(II)**

5.13 4.05 Cu(II) 3.17 2.09 p H 1.12 Fig. 2. Effect of pH on the removal of Cu2+

15**and Pb2+ ions from** single and binary **solutions.** Increasing **pH of the solution** above the pHpzc **of the**

solid facil- itated the sorption process. This is

16**due to the** increased **negative charge** density **on the** biosorbent **surface** because **of the**

dissocia- tion of carboxylic acids to carboxylate anions (R-COO ) that took

23**place in** a **pH range between 3.** 5 **and 5.**

5, which is the range of acid dissociation value (pKa) of carboxylic acids. Hence,

22**an electrostatic attraction** force **between the** deprotonated solid **surface and** metal **ions**

occurred and facilitated biosorption process. Furthermore, the occurring competitions between metal ions and H+ for the adsorp- tion sites become weaker with increasing pH of the solution. 3.3.

14**Biosorption mechanism of Cu(II) and** Pb **(II) ions onto rice straw** When dealing with **the**

investigation of adsorption mechanism of adsorbate onto the adsorbent surface, the information regarding the shift of functional groups and the presence of new absorption bands can be used as valuable hints. The main constituents of rice straw namely lignin, cellulose, and hemicelluloses are known to be associated, in part, 13**hydroxyl, carboxyl, and phenol functional groups,** which **are** responsible in providing **the**

adsorption sites for metal ions. These oxygen-containing surface groups are pH- dependent hence the change in pH would affect the chemical state and charge density of these functionalities. As explained above, when

22**pH of** the **solution was** above **pHpzc of**

the biosorbent, the surface functional groups of biosorbent were deprotonated and negatively charged ligands were formed. Conversely, the surface groups were protonated by hydronium ions when pH of the solu- tion was below the pHpzc of biosorbent, bearing a positive charge on the solid surface which tends to repulse the cationic-type adsorbates. The first stage of metal biosorption process was the deprotona- tion of hydroxyl group in carboxyl and phenol functionalities to form negatively charged hydroxylate and carboxylate sites. The next stage was the release of hydration waters from the hydrated metal ions, leaving the non-solvated cationic species in the solu- tion. The last stage was the uptake of non-solvated metal ions through electrostatic attractive forces between these species and negatively charged carboxyl or phenol oxygen atoms. Among the three stages above, the role of pH was remarkably important in the first stage because it governed the protonation and deprotona- tion of surface functionalities and the chemistry of metal species. Meanwhile, the sorption mechanism of copper and lead ions onto rice straw surface in binary mixture was essentially similar to that of single component system, except for the occurring competition between each metal species for the adsorption sites. 3.4. Modeling of adsorption isotherms 3.4.1. Single component system The information of the equilibrium relationship between the concentration of adsorbate in the liquid phase and adsorbed phase, also known as the adsorption isotherms is of great importance in the adsorption studies, not only for the design purpose, but also in understanding the adsorption equilibria, kinetics, and thermo- dynamics of single and multicomponent systems. In this regard, two adsorption models namely Langmuir and Freundlich were used to evaluate adsorption equilibrium data of single component system. Langmuir developed an adsorption theory based on the ki- netic principle and proposed the monolayer surface adsorption on the ideal solid with definite localised sites that energetically iden- tical [27]. This model further assumes that the adsorbate molecules can only accommodate one localised site without lateral interac- tions

15**between the adsorbed molecules, even on** the **adjacent sites.** Graphically, **Langmuir isotherm**

is characterized by a plateau curve, which means that no further adsorption can be occurred when equilibrium established. Originally, this empirical model was developed for describing adsorption phenomena in the gas phase but it had been extensively used for the correlation of adsorption equilibrium data of various solute-sorbent interactions in the liquid phase [19

24–**21]. The** mathematical **form of Langmuir isotherm** model **is given as** follows: KL **Ce qe**

¼ qm 1 þ KL Ce ð4Þ where qm is the maximum adsorptive capacity of the solid (mmol/ g), corresponds to the monolayer surface coverage (i.e. the adsor- bate layer is one molecule in thickness) and KL is Langmuir con- stants of adsorption affinity (l/mmol). As the value of Ce becomes

4**lower, the term** of KL **Ce is much less than unity and Langmuir** iso- therm **will obey Henry's law behavior. In contrast, when the value** of Ce **getting higher, the saturation point of adsorption will be reached and the concentration of solute on the solid surface will be equal to the maximum sorption capacity. The essential** charac- teristic **of Langmuir isotherm on the adsorption nature can be** as- sessed **by**

following equation [28]: RL ¼ 1 ð5Þ 1 þ KL C0 where RL

4**is a dimensionless equilibrium parameter or the** separa- tion **factor** and C0 is **the initial concentration of metal solution (mmol/l). The value** of RL **denotes the adsorption nature to be** unfa- vorable **(RL > 1), favorable (0 < RL < 1), irreversible (RL = 0), or linear (RL = 1).**

The second adsorption model used was Freundlich. Freundlich [29] proposed an empirical adsorption model on the solid with non-ideal nature, i.e. the adsorption energy and affinity are varied over the surface. This isotherm is not restricted to only monolayer surface adsorption and can be used adequately for describing the adsorption behavior in heterogeneous systems, particularly for the adsorption of organic matters by activated carbons, molecular sieves, and other solids with a complex structure. Freundlich iso- therm model has a mathematical form as follows: qe ¼ KF C1e=n ð6Þ Here, KF and n are Freundlich constants of adsorption

9**affinity ((mmol/g)** (mmol **/L) n) and** degree of **heterogeneity** of **the**

system, respectively. Higher value of n indicates a greater degree of hetero- geneity and the system increasingly deviated from linear isotherm. When n value was higher than about 10, the system approached a rectangular or non-reversible isotherm [30]. Generally, Freundlich isotherm agreed well in a narrow range of adsorption data, typically at moderate concentrations because this isotherm does not have

5**Henry's law** limit **at low concentration and** saturation **limit at high-**

end concentration. Moreover, this isotherm assumes that an infinite amount of adsorption can be occurred (i.e. the concentra- tion of solute on the solid surface continues to rise with increasing concentration

3**in the liquid phase), which means that no**

saturation limit at high-end concentration. The plots of biosorption equilibrium data of

16**Cu(II) and** Pb **(II) ions** at various temperatures **are** displayed **in Fig. 3. The** parameter values of **the**

models

12**were determined by nonlinear regression** fit- ting **using SigmaPlot software (Version 12.3, Systat Software Inc.) and the results are**

given

3**in Table 2.** In Fig. 3, **it can be seen that both** Langmuir **and**

Freundlich models can correlate experimental data satisfactorily with coefficient of determination (R2) approach- ing unity. However, a deeper analysis of the model, associated with justification of the physical meaning of the model parameters should be conducted. The affinity constants of solute toward the solid surface (i.e. KL and KF) were increased at higher temperatures, indicating that high temperature facilitated the sorption process. This is due to greater kinetic energy in the system that caused the molecules to move around faster and increase the adsorptivity 0.06 30 C o 0.05 40 oC 50 oC qe (mmol/g) 0.04 60 oC Langmuir Freundlich 0.03 0.02 0.01 Cu(II) - Rice straw 0.00 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 Ce (mmol/l) 0.045 30 oC 0.036

9**40 oC 50 oC 60 oC** qe **(mmol/g)**

0.027 Langmuir Freundlich 0.018 0.009 Pb(II) - Rice straw 0.000 0.0 0.1 0.2 0.3 0.4 Ce (mmol/l) Fig. 3. Biosorption isotherm plots of Cu2+ and Pb2+ ions at various temperatures. of solute. Because the Pauling electronegativity of Pb2+ ion is great- er than Cu2+ ion (i.e. 2.33 vs. 1.95) and the ionic size of the former is larger than the latter (i.e. 1.19 Å vs. 0.73 Å) [31], a stronger elec- trostatic interaction between Pb2+ ion and deprotonated carboxyl and hydroxyl surface functionalities was expected hence Pb2+ ion was preferentially adsorbed than Cu2+ ion. Similar behavior was observed for the maximum uptake

1**capacity of the solid at higher temperatures.** The qm values **for**

Cu2+ and Pb2+ ions at 60 °C were 0.0891 mmol/g (5.66 mg/g) and 0.1127 mmol/g (23.35 mg/g), respectively. As comparison, the maximum sorption capacities of several biomass-based sorbents for sequestering copper and lead ions from water and wastewater are listed in Table 3 [32–39]. With respect to RL values, all systems exhibit favorable biosorption nature. Moreover, the magnitude of all isotherm parameters obtained in this work agreed well with those reported previously in the literature for metal ion-biomass sorption systems [19–21,32,40]. As explained above, the movement of the molecules becomes faster at higher temperatures that increased the randomness de- gree of the system. This behavior was consistently described by Freundlich model, associated with the increasing value of n with temperature. Interestingly, it was also noted that the heterogeneity degree of Pb(II)-rice straw is lower than Cu(II)-rice straw at all temperatures. Through all analyses above, it can be concluded that the

33**Langmuir and** Freundich **models were** able **to** correlate bio- **sorption equilibrium data**

satisfactorily from both graphical and parameter justification point of view along with reasonable values of the fitted parameters. Table 2 The fitted Langmuir and Freundlich adsorption parameters for Cu(II)-rice straw and Pb(II)-rice straw at various temperatures. Ion T (°C) Langmuir qm (mmol/g) KL (l/mmol) Freundlich R2 RL KF (mmol/g) (mmol/l) n n R2 Cu2+ 30 40 50 60 0.0659 0.0753 0.0873 0.0891 0.5515 0.7618 0.8945 1.1244 0.99 0.99 0.99 0.98 0.53 0.46 0.42 0.36 0.0232 0.0325 0.0414 0.0478 1.33 1.46 1.52 1.62 0.99 0.99 0.99 0.99 Pb2+ 30 40 50 60 0.0740 0.0777 0.0899 0.1127 0.8646 1.3014 1.6526 1.8046 0.98 0.99 0.99 0.99 0.71 0.62 0.56 0.54 0.0417 0.0560 0.0746 0.0985 1.18 1.27 1.31 1.33 0.98 0.99 0.99 0.99 3.4.2. Binary component system In the present work, the biosorption

25**equilibrium data of Cu(II) and Pb(II) ions** from binary solution **were**

evaluated by selectivity extended-Langmuir model. Before moving further on the proposed model, it is necessary to discuss first the classical extended-Langmuir model that has a mathematical form as fol- lows [30]: qe;i ¼ qm;i 1 þ PKLnj;¼i1KCLe;;ii Ce;i ð7Þ For binary component system, Eq. (7) becomes: qe;1 ¼ qm;1 1 þ KL;1 K L;1 C e;1 Ce;1 þ KL;2 Ce;2 ð8Þ qe;2 ¼ qm;2 1 þ KL

5**;1 K L;2 C e;2** Ce **;1** þ KL **;2**

Ce;2 ð9Þ where qm,1, qm,2, KL,1 and KL,2 are the Langmuir adsorption parame- ters for single component system. In most cases, the

5**evaluation of binary adsorption data** by **extended-Langmuir model was** con- ducted **by**

comparing experimental and theoretical amounts of qe where the latter was calculated from Eqs. (8) and (9) by introducing the adsorption parameters for single system. Although this proce- dure can give satisfactory fitting results visually, however, it is lack of theoretical sounds since the adsorption behavior in single and binary systems are completely different. This can be explained by considering that the adsorptivity of solute and maximum surface coverage on the solid in single system are derived from pure com- ponent adsorption equilibria without any sorption interference from other solutes. Meanwhile, adsorption in binary component system involves the competition between adsorbate species for the active

18**functional groups on the adsorbent surface.** Such phenomenon **leads to the**

surface coverage on the solid by each adsorbate at certain fractional loadings. Hence, the adsorption parameters for single system can no longer be used to describe bin- ary adsorption data. For binary adsorption system, the aforesaid behaviors should be included in the correlation of experimental data. To address this point, we propose modification on the param- eters of

1**extended-Langmuir model (i.e.** qm **-bin and** KL **-bin)** that incor- porates **selectivity factor of the solute**

to describe the competitive adsorption in the system. The proposed qm and KL parameters of extended-Langmuir model for binary adsorption system are as follows: qm-bin ¼ qm;1-sinðC0;1 S21=C0;1 S21 þ C0;2 S12Þ þ qm;2-sinðC0;2 S12=C0;1 S21 þ C0;2 S12Þ KL;1-bin ¼ KL;1-sin expð S21Þ KL;2 bin ¼ KL;2-sin expð S12Þ ð10Þ ð11Þ ð12Þ where S is a dimensionless constant called selectivity factor or the ratio of affinity of each solute towards the solid surface and C0,i is the initial concentration of solute i in the mixture (mmol/l). The symbol S12 denotes the affinity of solute 1 (b1) relative to the affin- ity of solute 2 (b2) towards the solid surface and vice versa. Here, Cu and Pb ions were designated as solute 1 and solute 2, respectively. The exponential term was purposely used in order to describe the Langmuirian plots of adsorption isotherms (Ce vs. qe) in which the

27**concentration of adsorbate on the** solid **surface** rose exponentially **with** declining **concentration**

in the liquid phase and tend to be con- stant when equilibrium is getting closer to be reached. The mathe- matical relationship between KL and S can be explained by considering the competitive adsorption between solute 1 and solute 2 in the system. Accordingly, the adsorptivity of each solute to- wards the solid surface in binary adsorption system should be weaker than that in single system. This behavior also applies to the maximum sorption capacity of the solid which is the sum of maximum sorption capacity of each solute multiplied by the mole fraction of solute adsorbed. By introducing the proposed mathemat- ical forms of qm-bin and KL-bin (Eqs. (10)–(12)) into Eq. (7), the selec- tivity extended-Langmuir model for binary adsorption system was obtained: ðqm;1-sinðC0;1 ðb2=b1Þ=C0;1 ðb2=b1Þ þ C0;2 ðb1=b2ÞÞ þ qm;2-sinðC0;2 ðb1=b2Þ=C0;1 ðb2=b1Þ þ C0;2 ðb1=b2ÞÞÞKL;1-sin expð b2=b1ÞCe;1 qe;1 ¼ 1 þ KL;1-sin expð b2=b1ÞCe;1 þ KL;2-sin expð b1=b2ÞCe;2 qe;2 ¼ ðqm;1-sinðC0;1 ðb2=b1Þ=C0;1 ðb2=b1Þ þ C0;2 ðb1=b2ÞÞ þ qm;2-sinðC0;2 ðb1=b2Þ=C0;1 ðb2=b1Þ þ C0;2 ðb1=b2ÞÞÞKL;2-sin expð b1=b2ÞCe;2 1 þ KL;1-sin expð b2=b1ÞCe;1 þ KL;2-sin expð b1=b2ÞCe;2 ð13Þ ð14Þ

9**Table 3 The maximum** uptake **capacity of several** biomass-based sorbents **for**

Cu2+ and Pb2+ ions. Biomass Conditions qm (mg/g) Reference pH T (°C) Cu2+ Pb2+ Rice straw Barley straw Galaxaura oblongata Ulva lactuca Banana peel Crab shell 6 6 5 5 5.5 3 5.5 60 30 25 20 30 25 5.66 4.64 – – – 38.62 19.83 23.35 23.2 88.6 34.7 7.97 This study [32] [33] [34] [35] [36] Pine Cone Shell Tea fungal Garden grass 5 4 naa 25 25 Ambient 6.81 4.64 58.34 – – – [37] [38] [39] a na = Not available. In the case of single component system, i.e. C0,2 = 0 in Eq. (13) and C0,1 = 0 in Eq. (14), both equations will reduce to single Lang- muir isotherm. To test the validity of the proposed model, the fit- ting results between original and selectivity extended-Langmuir models against experimental data were compared as shown in Fig. 4-I–III. In these figures, the circle and triangle symbols repre- sented the concentrations of copper and lead ions in binary solu- tion, respectively. For binary adsorption system, the plot of the isotherm model should fit both experimental data points because the concentrations of both solutes in the liquid phase are in dy- namic balance with those in the adsorbed state at equilibrium. Fig. 4-I shows the fitting result between experimental (solid symbols) and theoretical amounts of qe (wire-mesh plots). As clearly seen, this procedure fails to give good correlation result, revealing the invalid use of Langmuir adsorption parameters of sin- gle system for the evaluation of binary adsorption equilibrium data. To give more evidence on this, the evaluation of experimental data by original extended-Langmuir model by nonlinear regression fitting is depicted

32**in Fig. 4-** II. **It** was found **that the fitted** parameter **values**

(KL,1, KL,2, qm,1, and qm,2) obtained for binary adsorption sys- tem deviate away than those in single system. In other hand, the proposed selectivity extended-Langmuir model with two fitted parameters (i.e. b1 and b2) satisfactorily representing experimental data in this work (Fig. 4-III). The fitting of selectivity extended-Langmuir model against adsorption equilibrium data of copper and lead ions from binary solution at various temperatures is displayed in Fig. 5. It can be 0.05 0.04 ) g / l o 0.03 m m ( q e 0.02 0.01 0.00 I 0.4 0.8 1.2 Ce - Cu(II) (mmol/l) C 11.6.2 e - 0.8 P b 0.4 ( II) 1.6 0.0 ) g / l o m m ( q e 0.012 0.010 0.008 0.006 0.004 0.002 0.000 II 0.4 0.8 1.2 Ce - Cu(II) (mmol/l) C 1.6 e 1.2 - 0.8 P b 0.4 ( II) 1.6 0.0 0.020 III Cu(II) Pb(II) 0.016 g/) 0.012 o l m ( m q e 0.008 1.6 e C 0.004 1.2 - P 0.8 b 0.4 ( I I ) 0.000 0.0 0.4 0.8 1.2 1.6 Ce - Cu(II) (mmol/l) Fig. 4. Comparison of the fitted models between original extended-Langmuir (I and II) and selectivity extended-Langmuir (III) against biosorption data of Cu2+ and Pb2+ ions in binary solution at 30 °C. T=30oC T=40oC 0.020 0.030 0.015 l / g ) m 0.010 o m ( q e 0.005 0.005 0.000 0.4 0.8 1.2 1.6 Ce - Cu(II)(mmol/L) 1.6 0.4 0.0 Ce 0.8 1.P2b(II) - 0.000 0.4 0.8 1.2 1.6 Ce - Cu(II)(mmol/L) 1.6 0.4 0.0 0.8 1.2b(II) C e - P 0.04 T = 50 o C 0.04 T=60oC 0.03 Cu(II) Pb(II) 0.03 ) g / l o l / g ) m 0.02 m m 0.02 o ( ( m q e q e 0.01 0.01 1.6 1.2 1.6 1.2 0.00 0.8 0.8 b (II) 0.4 0.4 0.8 0.00 0.4 - P 1.2 0.0 e -Pb(II) 0.4 C C 0.8 1.2 1.6 0.0 C e e -

36**Cu(II)(mmol/L) 1.6** Ce - **Cu(II)(**

mmol/L) 0.025 0.020 l / g ) m0.015 o ( m q e 0.010 Fig. 5. The fitted model of selectivity extended-Langmuir against biosorption data of Cu2+ and Pb2+ ions in binary solution at various temperatures. Table 4 The fitted selectivity extended-Langmuir model parameters for the biosorption of Cu2+ and Pb2+ ions from binary solution at various temperatures. T (°C) Fitted parameters Adsorptivitya qm-binb (mmol/g) R2 b1 b2 KL,1-bin (l/mmol) KL,2-bin (l/mmol) Synthetic effluents 30 40 50 60 Real effluent 30 0.0168 0.0276 0.0210 0.0309 0.0273 0.0341 0.0311 0.0367 0.0019 0.0032 0.1069 0.4698 0.1752 0.6593 0.2563 0.7426 0.3455 0.7713 0.1024 0.5523 0.0667 0.0756 0.0877 0.0934 0.0667 0.95 0.94 0.96 0.95 0.71 a Calculated from Eqs. (11) and (12). b Calculated from Eq. (10). seen that the model can correlate experimental data satisfactorily with coefficient of determination (R2) ranged between 0.94 and 0.96. The parameter values of b1 and b2 were determined by non- linear regression fitting until convergence and minimum standard error of the estimate achieved. From Table 4, it can be seen that the values of KL,2-bin are higher than KL,1-bin at all temperatures, indicat- ing that Pb(II) ion is more readily adsorbed onto rice straw surface than Cu(II) ion and the order of ion's affinity for the adsorption sites is consistent with the behavior in single system. At higher temperatures, the metal uptake process was more favorable due to enhanced affinity of each cation towards the biosorbent surface. Toward this end, the adsorptivities of both adsorbates in binary solution were lower than those in single system, revealing the competitive adsorption in the system. 3.5. Application of biosorption studies in real effluent The feasibility of rice straw for removing heavy metal ions was also tested using real effluent. The effluent was collected at the influent point from a wastewater treatment plant (WWTP) located in Rungkut Industrial area that contained various heavy metal ions with initial concentrations given in Table 5. Other components such as phenols, chlorides, nitrogen and sulfur compounds were also found in trace to moderate concentrations (1–100 mg/L). The

27**pH of the** effluent **was measured** by **a Schott** CG-825 digital **pH- meter and**

found to be 4.31. Total dissolved solids (TDS) and total solids (TS) in the effluent were determined by following APHA standard methods [41] and found to be 1527

32**mg/L and** 1912 **mg/ L, respectively. The** biosorption experiments **were** conducted in **a**

250 mL stop- pered conical flask containing 100 ml effluent at room temperature (around 30 °C) and pH 6 using biosorbent mass of 10 g. The mix- ture was then shaken at 100 rpm for 24 h to reach equilibrium. The characteristics of untreated and treated real effluents are listed in Table 5. It was found that the concentration of TDS in untreated effluent was unchanged after pH adjustment, indicating that the formation of metal hydroxide precipitates did not occur. The for- mation of metal hydroxide precipitates is essentially undesirable Table 5 The characteristics of untreated and treated real effluents. Parameters Untreated Treated Original After pH adjustment TDS (mg/l) TS (mg/l) pH 1527 1522 1912 1908 4.31 6.07 Concentration of metal ions (mmol/l) 1296 1658 5.21 % Removal Synthetic Real Pb 0.35 Cu 1.26 Cr 0.71 Mn 0.64 Zn 0.82 Cd 0.53 Hg 0.18 Ni 0.49 Fe 1.65 Total removal (%) 0.35 0.32 1.26 1.19 0.71 0.69 0.64 0.62 0.82 0.77 0.53 0.50 0.18 0.17 0.49 0.47 1.65 1.58 40.8 9.1 27.6 5.3 – 2.7 – 3.4 – 5.6 – 6.2 – 7.5 – 4.8 – 4.1 68.4 48.7 because it diminishes the concentration of free metal ions in the solution, leading to a lesser metal removal and physically change the characteristic of the effluent with respect to the increase of TSS (total suspended solids) and decreased TDS. By comparing the percentage

19**removal of Cu and Pb ions from**

synthetic (Cu + Pb + water) and real effluents, the latter gave lower value for the same experimental conditions (68.4% vs. 48.7%).

10**This is** likely **due to a** more intensive **competition** of solutes **for the** active **binding sites**

on the solid because more solute species are pre- sented in the adsorption system. Lower percentage removal of cop- per and lead ions from real effluent also attributed to the reduced affinity of both adsorbates toward the biosorbent surface. The adsorptivity of copper (KL,1) and lead (KL,2) metal ions in the multicomponent system (i.e. real effluents) should be lower than those of single and binary sorption systems. However, it was found that the affinity of Pb(II) ions in real effluent (see Table 4) was higher than that of binary effluent (Cu + Pb + water), which verifies that the proposed model failed to describe experimental data from the- oretical viewpoint. The inadequacy of the proposed model was also seen in Fig. 6, associated with a fairly poor value of the coefficient of determination (R2 = 0.71) of the fitted model against experimental results. Taking into account all of these, it can be concluded that the proposed selectivity extended-Langmuir model cannot corre- late experimental

25**adsorption data of Cu(II) and Pb(II) ions**

in real effluent satisfactorily.

12**A plausible explanation to this point is that the**

currently proposed model only considers the competitive adsorption between two adsorbates in the solution while in the real effluent; more than two adsorbates existing and a greater ex- tent of the sorption competition occurred. Hence, a different math- ematics model or further modification of the selectivity factor concerning n-components should be used in order to obtain a bet- ter correlation result. With regard to the percentage removal, the adsorptivity of me- tal ions toward the solid surface can be arranged from the highest to the lowest as follows: Pb > Hg > Cd > Zn > Cu > Ni > Fe > Mn > Cr. After biosorption, the concentration of total dissolved solids in un- treated effluent declined from 1522 mg/L to 1296 mg/L because of the removal of some amounts of

14**metal ions by rice straw. The pH of**

untreated effluent became more acidic after metal ions uptake (from 6.07 to 5.21), which may be ascribed to the release of pro- tons into the solution from the dissociation of carboxylic acids (R-COOH) into carboxylate anions (R-COO ). This phenomenon acts as a preliminary stage in the metal binding process onto rice straw. 0.016 Cu(II) Pb(II) ) 0.012 g l / o m ( m 0.008 q e 0.004 0.000 C 1.2 e - 0.8 P b (II) 0.4 0.0 0.0 100 80 l a o 60 v m e R % 40 20 0 Cu + Water 0.8 1.2 1.6 Pb + Water Cu - Pb + Water C0e.4- Cu(II) (mmol/l) Real 7 6 5 Cycle 4 3 2 1 Fig. 6. The correlation of biosorption data of Cu2+ and Pb2+ ions from real effluent by selectivity extended-Langmuir model (left-hand side) and stability tests of spent biosorbent (right-hand side).

3.6. Desorption study of spent biosorbent Regenerability is one of desired criteria of adsorbent in order to make the sorption process more economical, particularly for indus- trial practice and explore the possibility for recovering metal re- sources from the liquid phase. The regenerability of rice straw in this work was evaluated by subjecting the spent biosorbent to se- ven-successive adsorption–desorption cycles. Desorption experi- ments were performed at room temperature by mixing 1 g of metal-loaded rice straw with 50 mL eluent solution in a series of stoppered conical flasks for 24 h. The eluent solution used was di- lute hydrochloric acid at initial concentration of 0.1 M. The effect of recycling time on the stability performance of rice straw in seques- tering heavy metal ions from synthetic (Cu + water, Pb + water, and Cu + Pb + water) and real effluents is shown in Fig. 6. Experimental results (Fig. 6) show that the repeated use of bio- sorbent in the case of synthetic wastewaters still feasible for five cycles with comparable percentage removal against the previous cycle. Meanwhile, the regenerated

34**biosorbent can** only **be used** three times **for the** effective **removal of metal ions**

from real efflu- ent. After third cycle, the adsorption capacity of biosorbent started to decline drastically and no further desorption at the sixth cycle. A shorter life time of regenerated biosorbent in this case may be as- cribed to the difficulties in leaching some heavy metal ions that strongly bound in the solid matrices. Apart from this, all results above show the feasibility and potential application of rice straw for the treatment of metal-bearing effluents in large-scale operation. 3.7. Biosorption thermodynamics In order to gain a complete understanding on

31**the biosorption** nature **of Cu(II) and Pb(II)** ions **onto**

rice straw surface, thermody- namic aspects of the sorption process such as the standard enthal- py change (DH°), the standard entropy change (DS°), and the free energy change (DG°) were studied. These thermodynamic parame- ters can be evaluated by considering the variation of apparent equilibrium constant or sorption distribution (KD) with tempera- ture. The mathematical relationship between the equilibrium sorp- tion distribution and

11**free energy change of adsorption** can **be**

expressed by the classical van’t Hoff equation below: DG ¼ RT ln KD ð15Þ where DG°

11**is the Gibb’s free energy change (kJ/mol)** that measures **the**

11**spontaneity of a chemical reaction and**

can be expressed as 8.5 8.0 7.5 7.0 ln KD 6.5 6.0 5.5 5.0 4.5

19**Cu(II)** - single **Pb(II)** - single **Cu(II)** - binary **Pb(II)**

- binary van't Hoff plot 0.0030 0.0031 0.0032 0.0033 1/T (K-1) Fig. 7. The van’t Hoff plot for biosorption of Cu2+ and Pb2+ ions from single and binary systems. DG° = DH° TDS°, KD is the thermodynamic distribution coefficient that defined as a ratio of concentration of the solute in the adsorbed phase (mmol/l) to that in the liquid phase (mmol/l) at equilibrium,

26**R is the** universal **gas constant (8.314 J/mol K), and T is the** operating **temperature (K). The** parameter KD **can be**

35**obtained by plotting a straight line of In (qe/Ce)** vs. **qe and extrapolating qe to zero**

accord- ing to the Khan and Singh method [42]. The standard enthalpy change and standard entropy change of an adsorption process can be determined by substituting DG° = DH° TDS° into Eq. (15) to give the following van’t Hoff equation: lnKD ¼ DS0 DH0 R RT ð16Þ The values of DH° (kJ/mol) and DS° (kJ/mol K) can be calculated

28**from the** slope **and intercept of the linear plot of In** KD **vs. 1/T,** respectively. By evaluating **these parameters, the** nature of an **adsorption process**

can be known whether it is endothermic (DH° > 0), exothermic (DH° < 0), spontaneous (DG° < 0), or non-spontaneous (DG° > 0). The van’t Hoff plots

31**for the biosorption of copper and lead** ions **onto**

rice straw in single component system are depicted in Fig. 7 while the corresponding thermodynamic parameters are tabulated in Table 6. From Table 6, it can be known that the biosorption of Cu2+ and Pb2+ ions by rice straw are spontaneous and endothermic in nature with respect to the negative values of DG° and positive values of DH°. Increasing temperature led to a more negative value of DG°, indicating that higher temperatures energetically favor the feasibility and spontaneity of the biosorption process. This may be attributed to the faster mobility of solute molecules in the solution at elevated temperatures that enhanced their adsorptivity toward the biomass surface. By comparing the magnitude of DG° values for the biosorption of copper and lead ions at the same tempera- ture, it can be known that the biosorption of the latter species was more favorable than the former, which is consistent with the adsorption isotherm results. The endothermic behavior of the re- moval of copper and lead ions by rice straw revealed that an energy input (heat) is required for conducting the process and the rise in temperature increased the removal effectiveness and

5**maximum sorption capacity of the solute. In** addition, **the**

magnitude of DH° may also give an idea about the type of sorption process whether it is physisorption (i.e. 2

5**.1–20.9 kJ/mol) or** chemisorption (i.e. **80– 200 kJ/mol).**

As seen in Table 6, the values of DH° for the biosorp- tion of copper and lead ions using rice straw were 37.64 kJ/mol and 39.41 kJ/mol, respectively. These values do not fall into a range of

11**pure physical or chemical adsorption process,** which suggests **a** combination **of**

physisorption and chemisorption where the latter serves as the controlling mechanism. The positive values of DS° were observed for copper-rice straw and lead-rice straw systems, which reflected high preference of metal cations towards the adsorption sites and a random state

11**at the solid/solution interface with some structural changes in the adsorbate and**

biosorbent. Some explanations to this point were (1) the system gain more translational entropy

5**from the displacement of adsorbed water** molecules **by** metal cations; (2) **the**

release of hydration waters during the transition of metallic species; (3) higher mobility of the adsorbate molecules at elevated temperatures; and (4) the dis- tribution of translational and rotational energies during the self- orientation of adsorbate species in the adsorbed state. All these phenomena might be responsible, thus allowing for the prevalence of randomness in the system. For comparison purpose, the thermo- dynamic behavior of the biosorption of copper and lead ions using various kinds of biomass (besides rice straw) was given in Table 6 [34,43–45]. The thermodynamic behavior of

1**biosorption of copper and lead ions from** binary **solution**

can be determined by the same approach as of single component system [46]. It was found that the Table 6 Thermodynamic parameters for the biosorption of Cu2+ and Pb2+ ions by various biomass. Biomass Ion T (K) DG° (kJ/mol) DH° (kJ/mol) DS° (J/mol K) Reference Rice straw Cu2+ Pb2+ 303.15 313.15 323.15 333.15 303.15 313.15 323.15 333.15 14.29 16.00 17.71 19.43 16.48 18.33 20.17 22.01 37.64 39.41 171.29 184.37 This study Ulva lactuca Pb2+ 293.15 303.15 313.15 323.15 16.7 16.4 15.7 15.4 30.2 45.8 [34] Tannin resin Pb2+ 296 306 326 346 366 5.43 6.63 9.17 11.54 14.42 31.84 127.02 [43] Rubber leaf powder

Cu2+ 300 310 320 3.38 2.17 1.48 31.96 95.94 [44] Grafted chitosan bead Cu2+ 303 313 323 14.04 14.19 14.23 11.15 12 [45] spontaneity of the sorption process for both heavy metals from binary solution at all temperatures was diminished likely due to the competitive adsorption occurring between the ionic species in the liquid phase. The DG° values for biosorption of Cu2+ and Pb2+ ions were ranged from 12.51 kJ/mol to 16.32 kJ/mol and 13.27 kJ/mol to 19.31 kJ/mol, respectively. Conversely, the val- ues of entropy change for the removal of copper and lead ions from binary solution were higher that those of single metal removal (i.e. 190.52 J/mol K for Cu2+ and 201.20 J/mol K for Pb2+), reflecting a more irregular state at the solid/solution interface which might be associated with the presence of competing ion so the vacant sites on the solid surface were occupied by both components. The biosorption of Cu2+ and Pb2+ ions from their mixture was endo- thermic with enthalpy changes of 45.24 kJ/mol and 47.72 kJ/mol, respectively. Higher values of DH° mean that more energy is re- quired

18**for the metal** cations **to be adsorbed onto** biosorbent **surface** as a result **of**

competitive biosorption in the system. 4. Conclusions The utilisation and evaluation of rice straw for the removal of copper and lead ions from single and binary solutions have been demonstrated in this work. Some crucial implications of this study are listed below: The proposed selectivity extended-Langmuir model with two fitted parameters (b1 and b2) satisfactorily correlating biosorp- tion equilibrium data of Cu(II)APb(II) mixture at all tempera- tures compared to the classical extended-Langmuir model. The biosorption performance of rice straw for sequestering heavy metals from real effluent was fairly good with percentage removal of 48.7%. The utilisation of rice straw as a natural sorbent for heavy metal ions show potential application for scale-up purpose due to its abundance in nature, low cost, and reusability. Thermodynamically, the biosorption of copper and lead metal ions by rice straw from single and binary solutions was sponta- neous (DG° < 0) and endothermic (DH° > 0) with high prefer- ence of metal cations towards the biomass surface (DS° > 0). Acknowledgments This research was supported by the International Foundation for Science, Stockholm, Sweden, through a Grant to Felycia Edi Soetaredjo. References [1] K.P. Singh, D. Mohan, S. Sinha, R. Dalwani, Impact assessment of treated/ untreated wastewater toxicants discharged by sewage treatment plants on health, agricultural, and environmental quality in the wastewater disposal area, Chemosphere 55 (2004) 227–255. [2] K. Cheyns, S. Peeters, D. Delcourt, E. Smolders, Lead phytotoxicity in soils and nutrient solutions is related to lead induced phosphorus deficiency, Environ. Pollut. 164 (2012) 242–247. [3] L. Santorufo, C.A.M. Van Gestel, G. Maisto, Ecotoxicological assessment of metal-polluted urban soils using bioassays with three soil invertebrates, Chemosphere 88 (2012) 418–425. [4] A. Singh, S.M. Prasad, Reduction of heavy metal load in food chain: technology assessment, Rev. Environ. Sci. Biotechnol. 10 (2011) 199–214. [5] Y. Yi, Z. Yang, S. Zhang, Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin, Environ. Pollut. 159 (2011) 2575– 2585. [6] M.H. Yu, Environmental Toxicology-Biological and Health Effects of Pollutants, second ed., CRC Press, Boca Raton, Florida, 2005. [7] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41. [8] T. Kikuchi, S. Tanaka, Biological removal and recovery of toxic heavy metals in water environment, Crit. Rev. Env. Sci. Technol. 42 (2012) 1007–1057. [9] H. Bessbousse, T. Rhlalou, J.F. Verchere, L. Lebrun, Removal of heavy metal ions from aqueous solutions by filtration with a novel complexing membrane containing poly(ethyleneimine) in a poly(vinyl alcohol) matrix, J. Membr. Sci. 307 (2008) 249–259. [10] S.A. Abo-El-Enein, M.A. Eissa, A.A. Diafullah, M.A. Rizk, F.M. Mohamed, Utilization of a low cost agro-residue for production of coagulant aids and their applications, J. Hazard. Mater. 186 (2011) 1200–1205. [11] L. Charerntanyarak, Heavy metals removal by chemical coagulation and precipitation, Water Sci. Technol. 39

(1999) 135–138. [12] S. Malamis, E. Katsou, K. Takopoulos, P. Demetriou, M. Loizidou, Assessment of metal removal, biomass activity and RO concentrate treatment in an MBR-RO system, J. Hazard. Mater. 209–210 (2012) 1–8. [13] A. Stojanovic, B.K. Keppler, Ionic liquids as extracting agents for heavy metals, Sep. Sci. Technol. 47 (2012) 189–203. [14] S.A. Abo-Farha, A.Y. Abdel-Aal, I.A. Ashour, S.E. Garamon, Removal of some heavy metal cations by synthetic resin purolite C100, J. Hazard. Mater. 169 (2009) 190–194. [15] N. Das, R. Vimala, P. Karthika, Biosorption of heavy metals – an overview, Indian J. Biotechnol. 7 (2008) 159–169. [16] A. Demirbas, Heavy metal adsorption onto agro-based waste materials: a review, J. Hazard. Mater. 157 (2008) 220–229. [17] F. Widodo, S. Wahyono, Kecernaan bahan kering, kecernaan bahan organik, produksi VFA dan NH3 pakan komplit dengan level jerami padi berbeda secara in vitro, Indonesian J. Food Technol. 1 (2012) 1–15. [18] H. Gao, Y. Liu, G. Zeng, W. Xu, T. Li, W. Xia, Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste-rice straw, J. Hazard. Mater. 150 (2008) 446–452. [19] C.G. Rocha, D.A.M. Zaia, R.V.d.S. Alfaya, A.A.d.S. Alfaya, Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in industrial effluents, J. Hazard. Mater. 166 (2009) 383–388. [20] H. Muhamad, H. Doan, A. Lohi, Batch and continuous fixed-bed column biosorption of Cd2+ and Cu2+, Chem. Eng. J. 158 (2010) 369–377. [21] Y. Ding, D. Jing, H. Gong, L. Zhou, X. Yang, Biosorption of aquatic cadmium(II) by unmodified rice straw, Bioresour. Technol. 114 (2012) 20–25. [22] P.C.C. Faria, J.J.M. Orfao, M.F.R. Pereira, Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries, Water Res. 38 (2004) 2043–2052. [23] J.S. Han, J.S. Rowell, Chemical composition of fibers, in: R.M. Rowell, R.A. Young, J.K. Rowell (Eds.), Paper and Composites from Agro-Based Resources, CRC Press, New York, 1997, pp. 83–134. [24] R.H. Crist, J. Robert Martin, D. Carr, J.R. Watson, H.J. Clarke, D.R. Crist, Interaction of metals and protons with Algae. 4. Ion exchange vs adsorption models and a reassessment of scatchard Plots; ion-exchange rates and equilibria compared with calcium alginate, Environ. Sci. Technol. 28 (1994) 1859–1866. [25] S. Schiewer, B. Volesky, Modeling multi-metal ion exchange in biosorption, Environ. Sci. Technol. 30 (1996) 2921–2927. [26] S.K. Papageorgiou, E.P. Kouvelos, E.P. Favvas, A.A. Sapalidis, G.E. Romanos, F.K. Katsaros, Metal-carboxylate interactions in metal-alginate complexes studied with FTIR spectroscopy, Carbohydr. Res. 345 (2010) 469–473. [27] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403. [28] T.W. Weber, R.K. Chakravorti, Pore and solid diffusion models for fixed-bed adsorbers, AIChE J. 20 (1974) 228–238. [29] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem. 57 (1906) 385–470. [30] D.D. Do, Adsorption Analysis: Equilibria and Kinetics, first ed., Imperial College Press, London, 1998. [31] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Crystallogr. A 32 (1976) 751–767. [32] E. Pehlivan, T. Altun, S. Parlayici, Utilization of barley straws as biosorbents for Cu2+ and Pb2+ ions, J. Hazard. Mater. 164 (2009) 982–986. [33] W.M. Ibrahim, Biosorption of heavy metal ions from aqueous solution by red macroalgae, J. Hazard. Mater. 192 (2011) 1827–1835. [34] A. Sari, M. Tuzen, Biosorption of Pb(II) and Cd(II) from aqueous solution using green alga (Ulva lactuca) biomass, J. Hazard. Mater. 152 (2008) 302–308. [35] G. Annadurai, R.S. Juang, D.J. Lee, Adsorption of heavy metals from water using banana and orange peels, Water Sci. Technol. 47 (2003) 185–190. [36] S. Dahiya, R.M. Tripathi, A.G. Hegde, Biosorption of lead and copper from aqueous solutions by pre-treated crab and arca shell biomass, Bioresour. Technol. 99 (2008) 179–187. [37] G. Blazquez, M.A. Martin-Lara, E. Dionisio-Ruiz, G. Tenorio, M. Calero, Copper biosorption by pine cone shell and thermal decomposition study of the exhausted biosorbent, J. Ind. Eng. Chem. 18 (2012) 1741–1750. [38] R. Razmovski, M. Sciban, Biosorption of Cr(VI) and Cu(II) by waste tea fungal biomass, Ecol. Eng. 34 (2008) 179–186. [39] M.A. Hossain, H.H. Ngo, W.S. Guo, T. Setiadi, Adsorption and desorption of copper(II) ions onto garden grass, Bioresour. Technol. 121 (2012) 386– 395. [40] B. Singha, S.K. Das, Biosorption of Cr(VI) ions from aqueous solutions: kinetics, equilibrium, thermodynamics and desorption studies, Colloids Surf. B 84 (2011) 221–232. [41] APHA,

Standard Methods for the Examination of Water and Wastewater, 18th ed., American Public Health Association, Washington, DC, 1998. [42] A. Khan, R. Singh, Adsorption thermodynamics of carbofuran on Sn(IV) a rsenosilicate in H+, Na+, and Ca+ forms, Colloids Surf. 24 (1987) 33–42. [43] M. Yurtsever, I.A. Sengil, Biosorption of Pb(II) ions by modified quebracho tannin resin, J. Hazard. Mater. 163 (2009) 58–64. [44] W.S.W. Ngah, M.A.K.M. Hanafiah, Adsorption of copper on rubber (Hevea brasiliensis) leaf powder: kinetic, equilibrium, and thermodynamic studies, Biochem. Eng. J. 39 (2008) 521–530. [45] M.R. Gandhi, G.N. Kousalya, N. Viswanathan, S. Meenakshi, Sorption behavior of copper on chemically modified chitosan beads from aqueous solution, Carbohydr. Polym. 83 (2011) 1082–1087. [46] G. Uslu, M. Tanyol, Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead(II) and copper(II) ions onto Pseudomonas putida: Effect of temperature, J. Hazard. Mater. 135 (2006) 87–93. Author's personal copy 138 Author's personal copy F.E. Soetaredjo et al. / Chemical Engineering Journal 219 (2013) 137–148

3**Author's personal copy** F.E. Soetaredjo **et al. / Chemical Engineering Journal**

219 (2013) 137–148 139 140

3**Author's personal copy** F.E. Soetaredjo **et al. / Chemical Engineering Journal**

219 (2013) 137–148

3**Author's personal copy** F.E. Soetaredjo **et al. / Chemical Engineering Journal**

219 (2013) 137–148 141 142

3**Author's personal copy** F.E. Soetaredjo **et al. / Chemical Engineering Journal**

219 (2013) 137–148

3**Author's personal copy** F.E. Soetaredjo **et al. / Chemical Engineering Journal**

219 (2013) 137–148 143 144

3**Author's personal copy** F.E. Soetaredjo **et al. / Chemical Engineering Journal**

219 (2013) 137–148

3**Author's personal copy** F.E. Soetaredjo **et al. / Chemical Engineering Journal**

219 (2013) 137–148 145 146

3**Author's personal copy** F.E. Soetaredjo **et al. / Chemical Engineering Journal**

219 (2013) 137–148

3**Author's personal copy** F.E. Soetaredjo **et al. / Chemical Engineering Journal**

219 (2013) 137–148 147 148 Author's personal copy F.E. Soetaredjo et al. / Chemical Engineering Journal 219 (2013) 137–148