Turnitin Originality Report

CEJ11027 by Suryadi Ismadji

From journal (Hippo-hippo)

Processed on 15-Feb-2018 22:36 WIB
ID: 916458903
Word Count: 6747

Similarity Index	Similarity by Source	
19%	Internet Sources:	13%
	Publications:	19%
	Student Papers:	7%

sources:

1 2% match (student papers from 24-Jan-2014)
Submitted to Seoul National University on 2014-01-24

2 1% match (publications)
Ahmaruzzaman, Md.. "Adsorption of phenolic compounds on low-cost adsorbents: A review", Advances in Colloid and Interface Science, 20081104

3 1% match (publications)
Chandra, T.C.. "Adsorption of basic dye onto activated carbon prepared from durian shell: Studies of adsorption equilibrium and kinetics", Chemical Engineering Journal, 20070301

4 1% match (Internet from 06-Oct-2014)
http://140.118.33.11/handle/987654321/58?page=8

5 1% match (publications)
Prahas, D.. "Activated carbon from jackfruit peel waste by H"3PO"4 chemical activation: Pore structure and surface chemistry characterization", Chemical Engineering Journal, 20080701

6 1% match (publications)
A. Dąbrowski, P. Podkościelny, Z. Hubicki, M. Barczak. "Adsorption of phenolic compounds by activated carbon—a critical review", Chemosphere, 2005

7 1% match (Internet from 05-Sep-2013)
http://rsce2012.its.ac.id/search.php

8 1% match (publications)
Edi-Soetaredjo, Felycia, Suryadi Ismadji, and Yi-Hsu Ju. "Measurement and modeling of epicatechin solubility in supercritical carbon dioxide fluid", Fluid Phase Equilibria, 2013.

9 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.

10 1% match (student papers from 13-Jun-2011)
Submitted to National Chung Hsing University on 2011-06-13

11 1% match (Internet from 13-Oct-2016)
http://www.omicsonline.com/open-access/subcritical-water-extraction-of-xanthone-from-mangosteen-garcinia-mangostana-linn-pericarp-2090-4568-1000117.php?aid=44509

12 1% match (Internet from 01-Dec-2015)
http://www.jeaconf.org/UploadedFiles/Document/897510bf-1f90-4689-968c-40d7b71c0011.pdf

13 < 1% match (publications)
Ismadji, Suryadi, Felycia Edi Soetaredjo, and Aning Ayucitra. "The Kinetic Studies in the Adsorption of Hazardous Substances Using Clay Minerals", SpringerBriefs in Molecular Science, 2015.

14 < 1% match (Internet from 17-Nov-2014)
http://www.doria.fi/bitstream/handle/10024/100944/Sanna%20Hokkanen%20VK%2029%2010%20%20pdf%20kirjast
sequence=2

15 < 1% match (publications)
Zullaikah, S.. "A two-step acid-catalyzed process for the production of biodiesel from rice bran oil", Bioresource Technology, 200511

16 < 1% match (Internet from 22-May-2011)
http://asia.edu.tw/~ysho/Truth/PDF/App%20Cla%20Sci48,%2081.pdf

17 < 1% match (Internet from 12-Jul-2017)
http://journals.pan.pl/Content/81763/mainfile.pdf

18 < 1% match (publications)
Borneman, Z.. "Selective removal of polyphenols and brown colour in apple juices using PES/PVP membranes in a single ultrafiltration process", Separation and Purification Technology, 20010301

19 < 1% match (publications)
Anirudhan, T.S., J.R. Deepa, and Anoop S. Nair. "Fabrication of chemically modified graphene oxide/nano hydroxyapatite composite for adsorption and subsequent photocatalytic degradation of aureomycine hydrochloride", Journal of Industrial and Engineering Chemistry, 2016.

20 < 1% match (student papers from 11-Dec-2013)
Submitted to The University of Manchester on 2013-12-11

21 < 1% match (publications)
Anggraini, Merry, Alfin Kurniawan, Lu Ki Ong, Mario A. Martin, Jhy-Chern Liu, Felycia E. Soetaredjo, Nani Indraswati, and Suryadi Ismadji. "Antibiotic detoxification from synthetic and real effluents using a novel MTAB surfactant-montmorillonite (organoclay) sorbent", RSC Advances, 2014.

22 < 1% match (publications)

Rahardjo, A.K.. "Modified Ponorogo bentonite for the removal of ampicillin from wastewater", Journal of Hazardous Materials, 20110615

23 < 1% match (publications)
SHIRLENE M. ANTHONYSAMY. "BROWNING OF SAGO (METROXYLON SAGU) PITH SLURRY AS INFLUENCED BY HOLDING TIME, pH AND TEMPERATURE", Journal of Food Biochemistry, 5/2004

24 < 1% match (student papers from 15-Apr-2014)
Submitted to Stockholms universitet on 2014-04-15

25 < 1% match (Internet from 15-Dec-2015)
http://arjournals.org/index.php/ijpm/article/download/113/107

26 < 1% match (publications)
S.B. REVANAPPA. "PHENOLIC ACID PROFILES AND ANTIOXIDANT ACTIVITIES OF DIFFERENT WHEAT (TRITICUM AESTIVUM L.) VARIETIES : PHENOLIC ACID PROFILES IN WHEAT VARIETIES", Journal of Food Biochemistry, 05/2010

27 < 1% match (Internet from 12-Sep-2017)
http://ethesis.nitrkl.ac.in/7768/1/2016_MT_BajunHasanda_710CH1021.pdf

28 < 1% match (publications)
Muhammad, , T.G. Chuah, Yunus Robiah, A.R. Suraya, and T.S.Y. Choong. "Single and binary adsorptions isotherms of Cd(II) and Zn(II) on palm kernel shell based activated carbon", Desalination and Water Treatment, 2011.

29 < 1% match (Internet from 24-Sep-2014)
http://www.cyut.edu.tw/~ijase/2010/7(2)/2_016003.pdf

30 < 1% match (Internet from 21-Nov-2017)
http://upcommons.upc.edu/bitstream/handle/2117/96251/TJLV1de1.pdf?isAllowed=y&sequence=1

31 < 1% match (Internet from 18-Feb-2017)
http://users.csa.upatras.gr/~vgpapa/files/VGPpaper42.pdf

32 < 1% match (publications)
Wibowo, N.. "Adsorption of benzene and toluene from aqueous solutions onto activated carbon and its acid and heat treated forms: Influence of surface chemistry on adsorption", Journal of Hazardous Materials, 20070719

33 < 1% match (student papers from 06-Jun-2015)
Submitted to University of Sheffield on 2015-06-06

34 < 1% match (Internet from 18-Aug-2016)
http://benthamopen.com/FULLTEXT/TOCENGJ-10-18

35 < 1% match (Internet from 08-Sep-2017)
https://idus.us.es/xmlui/bitstream/handle/11441/27154/Tesis%20SMG_revFJGO.pdf?isAllowed=y&sequence=4

36 < 1% match (Internet from 28-Dec-2017)
http://www.philrice.gov.ph/wp-content/uploads/2017/12/Biology-and-management-of-invasive-apple-snails.pdf

37 < 1% match (publications)
Aksu, Z.. "Use of dried sugar beet pulp for binary biosorption of Gemazol Turquoise Blue-G reactive dye and copper(II) ions: Equilibrium modeling", Chemical Engineering Journal, 20070301

38 < 1% match (publications)
Jacobsen, S.. "Single-step reactive extrusion of PLLA in a corotating twin-screw extruder promoted by 2-ethylhexanoic acid tin(II) salt and triphenylphosphine", Polymer, 200004

39 < 1% match (Internet from 24-Sep-2017)
https://dr.ntu.edu.sg/bitstream/handle/10220/19432/Hybrid%20Multi-Walled%20Carbon%20Nanotubes-Alginate-Polysulfone%20Beads%20for%20Adsorption%20of%20Bisphenol-A%20from%20Aqueous%20Solution.pdf?isAllowed=y&sequence=1

40 < 1% match (publications)
Kosasih, A.N.. "Sequestering of Cu(II) from aqueous solution using cassava peel (Manihot esculenta)", Journal of Hazardous Materials, 20100815

paper text:

231

35**(2013)** 406–413 **Contents lists available at ScienceDirect Chemical Engineering Journal journal homepage: www.elsevier.com/locate/cej**

4**Recovery of catechin and epicatechin from sago waste effluent: Study of kinetic and binary adsorption isotherm studies** Felycia Edi **Soetaredjo** a, Suryadi **Ismadji** b, Shella Permatasari **Santoso** a, Ong Lu **Ki** b, Alfin **Kurniawan**

b,

7**Yi-Hsu** Ju **a,⇑** a **Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Sec 4., Keelung Rd., Taipei, Taiwan b Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia**

highlights

4**Recovery of catechin and epicatechin from sago waste effluent.** Supercritical CO2 desorption **of** catechin **and**

epicatechin from activated carbon. Adsorption of catechin and epicatechin in binary system.

24**article info Article history: Received** 27 May **2013 Received in revised form** 16 **July 2013 Accepted 17 July 2013 Available online 26 July 2013 Keywords:**

Catechin Epicatechin Binary adsorption Supercritical CO2 extraction abstract The recovery of valuable phenolic compounds (catechin and epicatechin) from sago waste effluent by activated carbon adsorption was studied in this work. Single and binary component of catechin and epi- catechin was studied in static mode using synthetic effluent.

37**Langmuir model was applied to** evaluate **the** adsorption **equilibrium data** in **single**

system. In binary system, the

21**modified extended Langmuir model** by **inclusion of surface coverage was**

used to represent the adsorption data. All experimental data were well represented either by Langmuir model or its modified form. For kinetic study, it was found that

16**pseudo-second order model** represents **the experimental data better than pseudo-first order model.**

Adsorption study using real sago waste effluent indicated that activated carbon adsorption process is promising for recovery of valuable phenolic compounds. Supercritical CO2 extraction of phenolic compounds from activated carbon resulted in low recovery. The addition of ethanol as co-solvent significantly enhanced the desorption of catechin and epicatechin from activated carbon. Ó 2013 Elsevier B.V. All rights reserved. 1. Introduction Phenolic compounds are universally distributed in plants such as leave, trunk, root, seed, and fruit. They are usually are bounded within plant tissues. Phenolic compounds as antioxidants are be- lieved

26**to contribute to health benefits through several possible mechanisms** such as **by quenching free radicals, chelating** transi- tion **metals, reducing peroxides and stimulating antioxidative** en- zyme **defense.**

25**Natural antioxidants are known to exhibit a wide range of biological effects including** anti-bacterial, **antiviral, anti- inflammatory, anti-allergic, antithrombotic and vasodilatory**

activ- ities [1]. The

17**antioxidant activity of** phenolic compounds **is mainly** attributed **to their redox properties, which allow them to act as reducing agents, hydrogen donors and** quenchers of **singlet** oxygen. In addition, **they may also** possess **metal chelating**

properties. Phe- nolic compounds possess aromatic structure along with hydroxyl ⇑

15**Corresponding author. Tel.: +886 (2) 2737** 6611; **fax: +886 (2) 2737 6644. E-mail address:** yhju@mail **.ntust.edu.tw (Y.-H. Ju).** 1385-8947/$ - **see front matter** Ó 2013 **Elsevier** B.V. **All rights reserved.** http://dx **.doi.**

org/10.1016/j.cej.2013.07.048 substituent

11**which enable them to protect human tissues from damages caused by oxygen or free radicals, and consequently** re- duce **the risk of** various **diseases, and offer beneficial** effect **against** cancer, **cardiovascular disease, diabetes, and Alzheimer's disease**

[2–7]. In starch extraction from sago pith, the sago pith slurry during sedimentation is browning due to the

23**oxidation of phenolic** com- pounds **by the polyphenol** oxidase (PPO) **enzyme** [8]. **Phenolic compounds are located mainly in vacuoles** while the **PPO** is found in plastids. Browning is initiated with the disruption of cell due to

23**cutting or bruising** and the **compartmentalization is lost. The**

pri- mary phenolic compounds related to browning are DL-epicatechin and D-catechin [8,9]. Pei-Lang et al. [9] reported that the content of phenolic compounds in sago pith depends on its growth stages and height; and the amount of phenolic compound extracted is less than 1%. Recovery of phenolic compounds from the waste effluents is beneficial, but it is a challenging process. Adsorption is efficient for removing

2**organic matter from waste effluents. Activated carbons are the most widely used adsorbents due to their** high **adsorption** capacities **for organic pollutants**

which are

2**related to their high surface area, pore volume and porosity. The adsorption**

capacities also

2**strongly depend on the activation method and the nature of source materials.**

2**Activated carbon is an effective** adsor- bent **for organic compounds removal, especially for phenolic**

com- pounds [10–15]. However, the utilization of activated carbon as adsorbent in the adsorption of epicatechin and catechin has never been reported. The focus of this work was to evaluate the adsorption perfor- mance of activated carbon for the recovery of epicatechin and cat- echin in single and binary component systems. The surface area was obtained based on Brunauer, Emmet, and Teller (BET) mea- surements, while the

31**pore volume and pore diameter of activated carbon were**

calculated from the adsorption experimental data using density functional theory (DFT). The effect of various vari- ables, such as initial adsorbate concentrations, adsorption time and mass of adsorbent were studied using batch equilibrium tech- nique. Pseudo first and second order kinetic models were used to correlate the adsorption dynamic or kinetic data. The

9**adsorption equilibrium data** was evaluated **using Langmuir model**

for single component, while modified extended-Langmuir model with incor- poration of solute’s selectivity factor was used to study the corre- lation [16]. The feasibility and adsorption performance of activated carbon in recovering epicatechin and catechin was also tested in real effluent. 2. Experimental section

8**2.1.** Chemicals **HPLC grade ( )-epicatechin (purity**

98 wt.%) and (+)-catechin hydrate (purity P 98 wt.%) were

8**obtained from Sigma Aldrich** (Sin- gapore) **and was used without any further purification.**

Pellet acti- vated carbon (0.5–1.5) produced by Norit (The Netherland) was used as the adsorbent. Double distilled water was used in adsorp- tion experiments. 2.2. Characterizations of activated carbon Since

5**structural heterogeneity of activated carbon plays an important role** during **adsorption**

therefore it is crucial to charac- terize the pore structure

3**of activated carbon. Pore** structure **of the activated carbon**

was characterized by nitrogen sorption tech- nique in a Quadrasorb SI at

36**boiling point of nitrogen gas (196 °C). Prior to the** nitrogen sorption measurement, **the** activated carbon was **degassed** in **vacuum** condition **at** 200 **°C** for 48 h. **The**

measure- ment of the nitrogen sorption isotherms (adsorption and desorp- tion) were conducted

40**over a relative pressure (p/po)** of **0.** 001– **0.** 990. **The BET surface area** of the carbon **was determined by**

stan- dard BET equation at a relative pressure of 0.06–0.3. Total of pore volume of the activated carbon was evaluated at the highest rela- tive pressure (0.990).

5**At this relative pressure all pores**

within the activated carbon were already completely filled with nitrogen gas.

5**Pore size distribution of the** carbon **was** determined **by** standard **DFT method** with **medium regularization.**

2.3. Static adsorption experiments The adsorbate solution was prepared by mixing a known amount of adsorbate (( )-epicatechin or (+)-catechin hydrate) with double distilled water to produce the desired initial concen- trations (100–150 mg/L). The adsorption was carried out isother- mally in static mode at 303.15 K. A fixed amount of activated carbon was added to

3**a series of 250 mL** glass-stoppered **flasks each filled with 100 mL**

diluted solutions. The glass stoppered flasks were then put in a thermostatic shaker bath at 120 rpm for 1 h (the equilibrium condition was achieved in about 40 min). The adsorption isotherm for binary systems of epicatechin and catechin was also obtained isothermally at 303.15 K, using the same proce- dure as for the single component adsorption. To study the adsorption kinetics,

3**a series of 250 mL** glass-stop- pered **flasks**

contained

3**100 mL of** phenolic compound **solution with** certain **initial concentration**

(100–250 mg/L) were prepared. Sub- sequently,

28**a known amount of activated carbon** (0.2 g) **was added into** each glass-stopper **flask. The**

glass-stopper flasks were placed in thermostatic water-bath shaker for 150 min at 303.15 K. During kinetic experiments, at intervals of 10 min, one of glass-stopper flask was taken and the concentration of phenolic compound was analyzed. The adsorption of phenolic compounds from waste effluent was carried out using waste water from sago starch extraction. Briefly, sago pith was pulverized into coarse powder and soaked in water (1 h), and then filtered using Buchner funnel to obtain the waste effluent. One gram of activated carbon was added to 250 mL glass-stopper

3**flasks each filled with 100 mL**

waste effluent. The glass stopper flask was placed in a thermostatic shaker bath at 120 rpm for 1 h. The initial and equilibrium concentrations of the single and bin- ary solutions and waste effluent were analyzed

8**using a HPLC (Jasco HPLC PU-2089 plus) with a UV–vis detector (UV-2077 plus)**

set at 280 nm. Separations were achieved in an Enduro C18, 5 lm, 250 4.6 mm. The flow rate was 0.8 ml/min. The mobile phase used was isocratic elution comprised of 3% acetic acid in double distilled water (60%) and acetonitrile (40%) for a total running time of 10 min. The contents of epicatechin and catechin were deter- mined using calibration curves. The effect of pH on the adsorption of epicatechin and catechin was investigated in single component systems. It was found that as the initial solution pH was reduced to pH 3, the solution concen- tration decreased up to 50% of the initial concentration. When the initial solution pH was increased to pH 10, the solution concentra- tion also decreased up to 60–70% of the initial concentration. This is due to oxidation of the phenolic compounds. Therefore, the adsorption of epicatechin and catechin in single and binary compo- nent were carried out at pH 7, which is similar to the waste effluent pH. 2.4. Calculations The amounts of epicatechin and catechin adsorbed onto acti- vated carbon in single component system were calculated using the following equation: qe ¼ ðC0 CeÞ m V ð1Þ where C0

> 20**and Ce are the initial and equilibrium concentration of** phenolic compounds **in** the **liquid phase (mg/L), respectively, V is the volume of** phenolic compounds **solution (L),** qe **is the** amount **of**

metal ions adsorbed per unit of biosorbent mass (mg/g), and m is the mass of activated carbon (g). The equilibrium concentration of phenolic compound i species (Ce,i) in binary mixture was calcu- lated by the same manner using following mass balance equation: qe;i ¼ ðC0;i Ce;iÞ m V ð2Þ where qe,i is the equilibrium amount of solute i in the adsorbed phase (mg/g), C0,i and Ce,i

> 21**are the initial and equilibrium** concentra- tion **of solute** i **in the liquid phase** (mg **/L), respectively.** All data are **the** average results **of**

triplicates experiments. 408 F.E. Soetaredjo et al. / Chemical Engineering Journal 231 (2013) 406–413 3. Results and discussion 70 3.1. Activated carbon characterization 60 Analysis of nitrogen sorption isotherms and DFT-pore size dis- tribution of the activated carbon used in this study indicates that the NORIT carbon possess both micropore and mesopore structures with micropore structure more dominant than mesopore as indi- cated by the rapid filling of pores at low relative pressure and fol- lowed by the gradual increase of adsorption at moderate relative pressure (S1). The existence of the mesopores is indicated by the presence of hysteresis loop between adsorption and desorption isotherms, an indication of capillary condensation in the mesop- ores. The

> 31**BET surface area,** micropore **volume, and** total **pore** vol- ume **of the activated carbon**

(NORIT nrs carbon Ea 0.5–1.5) were 890 m2/g, 0.431 cm3/g, and 0.506 cm3/g, respectively. The pore distribution of activated carbon

> 32**represents a model of** carbon **internal structure which**

represents non-interacting of reg- ularly shape model pores and

> 5**complex void spaces within the** car- bon. **The pore size distribution** of the carbon **is**

one of its most important characteristics of the carbon in studying adsorption equilibrium and kinetic. The

> 30**pore size distribution of the activated carbon** confirms that the **carbon**

possesses both micropore and mesopore structure (S2). 50 40 30 qe (mg.g-1) 20 10 0 0 20 25 20 qe (mg.g-1) 15 10 (a) 40 60 Ce (mg.L-1) 3.2. Adsorption isotherms 5 (b) The isotherm shape can be used as quasi-qualitative informa- tion

6**on the nature of the solute-surface interaction.** In **the** case **of** 0 **adsorption of** phenolic compounds **from**

water, it is characterized 40 50 60 70 80 90 100 by initial region (high uptake at low concentration); and Langmuir Ce (mg.L -1) model is best fitted for this case [17,18]. Based on the classification proposed by Giles et al. [17,18], the curve shape in Fig. 1 is class L2 Fig. 1. Adsorption isotherm of catechin and epicatechin onto activated carbon NORIT nrs carbon Ea 0.5–1.5 and Langmuir isotherm model (solid lines). according to the Giles classification

6**suggests that the aromatic ring** adsorbed is **parallel to the surface and no strong competition exists between the adsorbate and the solvent to occupy the adsorption**

time consuming and much more difficult to obtain. Therefore it sites [12].

14**Langmuir isotherm is characterized by a plateau curve**

will be convenient if the multi-component isotherm can be con- which indicates that equilibrium has been achieved. The Langmuir structed based on single adsorption isotherms. Various models isotherm was originally developed for describing gas adsorption have been developed for this purpose and one of the most widely phenomena but it has been extensively used for the correlation used is the extended Langmuir and its modified forms [16,22,23]. of

14**adsorption equilibrium data of various solute-sorbent** interac- **The**

extended Langmuir model for a two-component system can tions in liquid phase [19–21]. The Langmuir isotherm model is gi- be expressed as: ven as follows: qe ¼ qm 1 þKLKLCeCe ð3Þ qe;1 1 þ KqLm;1;C1Ke;1L;1þCKe;1L;2Ce;2 ¼ ð4Þ where qm

14**is the maximum** adsorption **capacity of the solid** (mg **/g)** corresponding **to monolayer surface coverage**

and KL is Langmuir qe;2 ¼ 1 þ KqLm;1;C2Ke;1L;2þCKe;2L;2Ce;2 ð5Þ constants of adsorption affinity (L/mg). where qm,i and Ce,i are the amount adsorbed and equilibrium con- Fig. 1 shows that the adsorption equilibrium data of phenolic centration of component i, respectively. The parameters qm,i and compounds are well fitted by the Langmuir isotherm model and KL,i are the adsorption capacity of component i in the adsorbent the correlation coefficients for epicatechin and catechin are 0.97 and adsorption affinity of component i, respectively. All these and 0.94, respectively. The maximum adsorption capacity (qm) of parameters are obtained from single adsorption isotherms. catechin (73.56 mg/g) obtained by fitting calculation using Sigma- In a multi-component system, competition for vacant adsorp- Plot 12.0 is higher than that of epicatechin (29.04 mg/g). The tion sites in the surface of adsorbent occurs not only between adsorption affinity parameter (KL) of catechin and epicatechin ob- the same molecules but also between different adsorbate species. tained are 0.1257 L/mg and 0.041 L/mg, respectively. Higher This competition may act as the controlling factor for the adsorp- adsorption affinity parameter of catechin than epicatechin indi- tion process [16,23] and such phenomenon is not captured by ori- cates that catechin is easier adsorbed onto the surface interior of ginal extended Langmuir model. Recently, Kurniawan et al. [23] the carbon. and Soetaredjo et al. [16] modified the extended Langmuir model Industrial Adsorption process usually involves multi-compo- by including fractional surface loading or coverage [23] and selec- nent, therefore, information on adsorption equilibria in multi-com- tivity factor [16]. Since both epicatechin and catechin are organic ponent system is required for engineering design of the adsorption compounds, the fractional surface loading approach by Kurniawan process. Compare to the single component adsorption, reliable et al. [23] is more

9**suitable to represent the** binary **adsorption** data **experimental**

multi-component adsorption isotherm data are more of this study. Since

30**competition between** catechin **and** epicatechin **molecules for** vacant **adsorption sites in the** activated **carbon** occurred during **the**

adsorption process, catechin and epicatechin were adsorbed in certain amount, and the adsorption capacity of the activated for both adsorbates (binary) can be written as qm;bin ¼ qm;1h1 þ qm;2h2 ð6Þ Here h1 and h2 are the fractional loading of catechin and epicatechin, respectively, and h1 + h2 = 1. The adsorption affinity parameter in Langmuir equation represents

9**how strong an adsorbate molecule is attracted onto** the **surface**

of the adsorbent. In a binary system, the competition between different molecules weakens the adsorp- tion potential

29**of the adsorbate** toward **the surface of adsorbent,** therefore, **the**

affinity parameter of binary compounds can be writ- ten as: KL;1ðbinÞ ¼ KL;1 exp KL;2ðbinÞ ¼ KL;2 exp h2 h1 ð7Þ h 1 h2 ð8Þ where KL,1(bin) and KL,2(bin) are the affinity parameter of catechin and epicatechin in binary system, respectively. The final expressions of extended Langmuir model with inclusion of fractional loading con- cept are qe;1 ¼ 1 þ KLq;1mðb;bininÞCKeL;;11ðþbinKÞCLe;2;1ðbinÞCe;2 ð9Þ qe;2 ¼ 1 þ KLq;1mðb;bininÞCKeL;;12ðþbinKÞCLe;2;2ðbinÞCe;2 ð10Þ The applicability of the modified extended Langmuir model was tested against the liquid phase binary adsorption data of catechin and epicatechin. The parameter è1 and è2 were obtained by the simultaneously fitting of Eqs. (9) and (10) using

34**nonlinear least square method by minimizing the following**

objective function 2 #0:5 SSE ¼ "P ðqexp qcalÞ n ð11Þ where qexp and qcal are the actual amount and the calculated values of catechin and epicatechin adsorbed by activated carbon, respec- tively;

34**n is the** total **number of experimental data** used in **the fitting**

procedure. Fig. 2 shows the 3D plots of binary adsorption of catechin and epicatechin at various initial concentrations and the model calcu- lated by Eqs. (9) and (10). The fitted parameters h1 and h2 with cal- culate values of qm,(bin), KL,1(bin), and KL,2(bin) are summarized in Table 1. In this work an improvement was made in the fitting pro- cedure of modified extended Langmuir model by Kurniawan et al. [23]. Both Eqs. (9) and (10) were simultaneously fitted by nonlin- ear least square method with h1 and h2 as the fitted parameters, with boundary condition of the fitting procedure as h1 + h2 = 1. It is obvious that this fitting procedure

28**improved the** applicability **of the modified** extended **Langmuir model** in correlating **the** binary experimental data **of**

catechin and epicatechin as indicated in Fig. 2. The maximum amount of adsorbates adsorbed in binary system (qm(bin)) was lower than in single system (qm) due to the effect of molecular competition between both adsorbate molecules. This competition was accommodated in the modified extended Lang- muir by taking into account of fractional loading coverage. The fractional coverage of catechin (h1) and the maximum amount adsorbates adsorbed (qm(bin)) decreased with increasing initial epi- catechin concentration as shown in Table 1. This result is consis- (a) g/ g m,50 d r b e osd 40 s a dnu 30 op oc 20 m icl n o hepf 10 80 otnuo 0 a m 90 80 30 4050a6te0c7h0in,mg/L 20 Ce c Ce epicatech7i0n, mg/L60 50 10 adsorption experimental data of catechin adsorption experimental data of epicatechin modified extended Langmuir model (b) g/g m,35 d b e o r ds 30 a d s un 25 p o m o c 20 lic n o he 15 p 80 f o / L t g nu 10 o 40 m 140 a 130 120 Ce epicatechin11,m0g/L 20 e c6at0echin,m 100 C 90 adsorption experimental data of catechin adsorption experimental data of epicatechin modified extended Langmuir model Fig. 2. 3D plot of binary adsorption data and modified extended Langmuir model. (a)

18**Catechin 100 mg/L + epicatechin 100 mg/L,** (b) catechin **100 mg/L** + epicatechin 150 **mg/L.**

tent with adsorption characteristics in single adsorption system that the adsorption capacity of epicatechin is less than that of cat- echin, therefore increasing the concentration of epicatechin in bin- ary system caused the interaction of adsorbate molecules to become even higher and reduce the value of qm(bin) . 3.3. Adsorption kinetics The effective design of an adsorption system requires informa- tion about the rate at which the organic compounds removal takes place in a given sorbent/solution system. Several adsorption kinetic

13**models have been developed to describe the** adsorption **kinetics** in liquid phase. **The**

development of adsorption kinetic models mostly is based on fundamental approach to interfacial kinetics and its modifications [24]. Several models which have been developed 410 F.E. Soetaredjo et al. / Chemical Engineering Journal 231 (2013) 406–413 Table 1 Fitted and calculated parameters for catechin and epicatechin adsorption at several initial concentrations. Phenolic compounds mixture Fitted parameter Calculate parameter R2 h1 h2 qm,(bin), mg/g KL,1(bin), L/mg KL,2(bin), L/mg

18**Catechin 100 mg/ L + Epicatechin 100 mg/L** Catechin **100 mg/ L** + Epicatechin 150 **mg/L**

0.632 0.368 0.524 0.476 57.1 0.0699 52.2 0.0499 0.0075 0.0139 0.998 0.997 based on this approach are Langmuir kinetics, first and second or- der, reversible first and second order, and irreversible reactions [24]. Another approach which is used to develop the kinetic mod- els is based on assuming that surface reaction is the rate control- ling step in sorption. Many simple and compact models have been proposed based on this approach and the famous and

39**widely used models** are **pseudo-first** (Lagergren) **and pseudo-second order** [24]. **Pseudo-first order model** which **is** also known **as**

Lagergren equation is the earliest empirical model describing the rate of adsorption in a liquid phase system [25]. The differential form of this model is dqðtÞ dt ¼ k1ðqe qðtÞÞ ð12Þ The

29**integration of Eq.** (12) **with initial** conditions: **q(t) = 0 at t = 0**

gives qðtÞ ¼ qeð1 expð k1tÞÞ ð13Þ where q(t)

33**is the amount of adsorbate adsorbed at time t (mg/g),** and **k1 is the rate constant** (1/min). **Pseudo-** second **order**

was first proposed by Blanchard et al. [26]. This model assumes that direct adsorption/desorption (seen as chemical reaction) is the rate controlling step in the overall sorp- tion kinetics [24], and has the differential form as dqdðttÞ ¼ k2ðqe qðtÞÞ2 ð14Þ Here

3**k2 is rate constant of pseudo-second order (g/mg min).** Inte- gration of **Eq.** (14) gives **the**

following result qðtÞ ¼ qe 1 þk2kq2etqet ð15Þ To obtain the parameters of pseudo-first and pseudo-second or- der equations, non-linear least square method was employed by fitting the kinetic experimental data with Eqs. (13) and (15) and the results are summarized in Table 2. Figs. 3 and 4 present the plots of catechin and epicatechin uptake as the function of time, respectively. The symbols represent the kinetic experimental data while the solid lines represent the pseudo-first and pseudo-second order kinetic models. As shown in Table 2, the values of R2 ob- tained from the fitting of kinetic experimental data using both models were similar, however the

16**pseudo-second order** kinetic **model represents kinetic** experimental **data better than the** pseu- do **-first order** since **the**

predicted amount of adsorbate adsorbed in equilibrium condition was closer to that of the measured one. This is confirmed by the fact that from the values of fitting param- eter qe of pseudo-second order model agree with the values of qe from kinetic experimental data. As mentioned by Plazinski et al. [24] that one of the potential advantages of using pseudo-second order kinetic model to correlate the adsorption kinetic experimen- tal data

13**is its small sensitivity to the influence of the random experimental error,**

especially for the fitting parameter qe. Another advantage of using

13**the pseudo-second order** is that **the value of** fit- ted **parameter**

qe can be obtained from the independent plot of ki- netic adsorption experimental data [24,27]. In many adsorption kinetic studies [24,27–29], failure of the pseudo-first order in correlating adsorption kinetic experimental data is due to the theoretical interpretations of this equation. In pseudo-first order it is based on the common assumption that the overall sorption process is controlled by the rate of adsorp- tion/desorption processes which is seen as a chemical reaction on the surface of adsorbent [24]. However in many cases, the rate of diffusion of solute into interior of the adsorbent also controls the adsorption mechanism and this phenomenon is not captured by the pseudo-first order model. Table 2, Figs. 3 and 4 clearly indicate that the parameter k2 plays a role as time scaling factor. At high k2, shorter time is required to reach equilibrium. As can be seen in Table 2, k2 decreased with increasing initial concentration. A simple correlation between of k 2 and initial concentration of the adsorbate (Co) is given as follows: k2 ¼ k2;o þ a expð bCoÞ ð16Þ where k2,o, a and b are empirical constants. Plots of Co versus k2 are given in Fig. 5. The fitted empirical constants for catechin are k2,o = 0.0013 g/mg min, a = 0.0194 g/mg min, and b = 0.0092 L/mg, while for epicatechin are k2,o = 0.0004 g/mg min, a = 0.0147 g/ mg min, and b = 0.0207 L/mg. Table 2 Fitted parameters of pseudo-first and pseudo-second order of catechin and epicatechin adsorption onto activated carbon NORIT nrs carbon Ea 0.5–1.5. Phenolic compound Co,

19**mg/L qe, mg/g,** experiment **Pseudo-first order Pseudo-second order k1,** 1 **/min qe, mg/g R2 k2, g/mg min qe, mg/g R2**

Catechin 101.3 122.5 139.8 158.7 203.6 251.9 Epicatechin 100.5 118.4 141.2 161.5 201.7 252.3 43.3 43.9 44.5 44.7 45.3 46.1 0.0631 0.0471 0.0441 0.0337 0.0275 0.0185 21.2 21.9 23.2 25.4 28.2 28.9 0.1037 0.1096 0.0974 0.0795 0.0708 0.0656 39.1 38.6 38.3 38.2 35.6 33.6 0.996 0.997 0.998 0.998 0.996 0.994 19.6 22.2 21.1 22.5 25.4 26.5 0.993 0.996 0.996 0.995 0.994 0.995 0.0022 0.0014 0.0013 0.0008 0.0007 0.0004 43.4 44.3 44.3 46.1 44.2 45.1 0.0086 0.0083 0.0069 0.0053 0.0040 0.0034 20.9 23.6 22.8 24.5 27.9 29.3 0.997 0.998 0.999 0.998 0.997 0.996 0.994 0.998 0.996 0.996 0.997 0.995 50 (a) 40 qt (mg.g-1) 30 20 10 0 0 20 40 60 80 100 120 140 160 T (min) 50 (b) 40 qt (mg.g-1) 30 20 10 0 0 20 40 60 80 100 120 140 160 T (min) Fig. 3. Kinetic adsorption experimental data of catechin onto activated carbon NORIT nrs carbon Ea 0.5–1.5 at various initial concentration and plots of

27**(a) pseudo- first order, and (b) pseudo-second order.** 3.4. Recover **of**

phenolic compounds in sago waste effluent To verify the potential application of recovering phenolic com- pounds from sago waste effluent by adsorption, adsorption exper- iments using real sago waste effluent were also conducted. The adsorption of catechin and epicatechin from real sago waste efflu- ent was conducted isothermally at 303.15 K under static condition. Prior to the adsorption experiment, the sago waste effluent was fil- tered to remove solid particles. The initial concentration of cate- chin and epicatechin in sago waste effluent was 321.8 mg/L and 158.2 mg/L, respectively. The recovery of catechin and epicatechin in sago waste effluent is

32**given in Table** 3. **From Table** 3 **it can be seen that the** recovery **of**

both phenolic compounds increases with increasing activated carbon mass due to the increase of adsorption active sites. At an adsorbent dose of 2%, the

4**recovery of catechin and epicatechin from sago waste effluent**

was 85% and 53%, respec- tively. It can be seen that the amount of phenolic compounds ad- sorbed by the activated carbon from real waste sago effluent (Table 3) is less than that of the synthetic one (Fig. 2). In waste sago effluent, in addition to catechin and epicatechin other compounds such as protein and soluble starch are also present which compete for adsorption active sites

22**resulting in the** observed decrease **of adsorption capacity**

toward catechin and epicatechin.

22**Reusability of adsorbent is crucial in industrial** application. **The**

recovery of catechin and epicatechin from activated carbon was performed by supercritical CO2 at 313.15 K and 26 MPa under sta- tic and dynamic conditions. Details about the supercritical system can be found elsewhere [30]. At static condition, the recovery of catechin from activated carbon was only 1.2% while for epicatechin it was 14.5%. This low recovery is consistent with the solubility 30 (a) 25 20 qt

12**(mg.g** -1) **15 10 5 0 0 20 40 60 80 100** 120 140 160 **T (min)**

30 (b) 25 20 qt

12**(mg.g** -1) **15 10 5 0 0 20 40 60 80 100** 120 140 160 **T (min) Fig. 4.**

Kinetic adsorption experimental data of epicatechin onto activated carbon NORIT nrs carbon Ea 0.5–1.5 at various initial concentration and plots of

27**(a) pseudo- first order, and (b) pseudo-second order.** data **of**

both phenolic compounds in supercritical CO2 under static condition [30,31]. In order to increase the recovery of catechin and epicatechin in supercritical CO2, dynamic extraction experiments were also conducted with flow rates of CO2 from 0.1 to 1 kg/h. By increasing CO2 flow rate from 0 kg/h (static mode) to 0.1 kg/h, the recovery increased from 1.2% to 2.3% and from 14.5% to 27% for catechin and epicatechin, respectively. Maximum recovery (catechin 9.7% and epicatechin 87.3%) was achieved

38**at a** CO2 **flow rate of 0.** 7 **kg/h.**

Further increase of CO2 flow rate to 1 kg/h had neg- ligible effect on the recovery both compounds. 0.010 0.008 Catechin Epicatechin k2, g/mg.min 0.006 0.004 0.002 0.000 80 100 120 140 160 180 200 220 240 260 Initial concentration, mg/L Fig. 5. Correlation between Co and k2. 412 F.E. Soetaredjo et al. / Chemical Engineering Journal 231 (2013) 406–413 Table 3 Adsorption of catechin and epicatechin from sago waste effluent. Co,1 catechin, mg/ Co,2 epicatechin, mg/ m, mass of activated carbon, L L g Ce,1, mg/ Ce,2, mg/ L L qe,1, mg/ qe,2, mg/ % Recovery g g catechin % Recovery epicatechin 321.8 158.2 0.112 0.483 0.689 0.921 1.104 1.328 1.573 1.921 274.4 143.3 141.2 113.8 110.3 103.8 99.8 100.2 95.5 96.4 85.4 93.1 71.2 87.4 48.3 74.2 42.3 13.3 37.4 9.2 30.7 7.9 24.1 6.3 20.5 5.6 17.8 4.9 15.9 4.5 14.2 4.3 14.7 9.4 56.1 28.1 65.7 34.4 68.9 36.7 70.3 39.1 73.5 41.1 77.7 44.7 84.8 52.3 Note: volume of sago waste effluent 100 mL. Low recovery of phenolic compound, especially catechin is caused by the difference in the polarity between the solute (pheno- lic compound) and the solvent (supercritical CO2). Catechin is highly polar while supercritical CO2 is non-polar. In order to in- crease the polarity of supercritical CO2, ethanol as co-solvent (5– 25%) was used in this study. By adding 5% ethanol

38**at a** CO2 **flow rate of 0.** 7 **kg/h,**

the recovery of catechin increased almost two fold (from 9.7% to 18.2%), and while for epicatechin the recovery reached 95.7%. Increasing the percentage of co-solvent increased the recovery of both compounds. For epicathecin the maximum recovery was 99.2% at 20% of co-solvent. Further increase in co-sol- vent concentration had negligible effect on the recovery of epicat- echin. The un-recovered epicatechin may be strongly bound on carbon surface or epicatechin molecule may be adsorbed inside small or ultra micropore so it could not be desorbed by supercrit- ical CO2. At 30% co-solvent, the recovery of catechin was 93.1%. Since further increase of co-solvent concentration changed super- critical condition into subcritical, therefore maceration (303.15 K, 24 h) was used to obtain maximum removal of catechin (97.8%) and epicatechin (99.4%). 4. Conclusion The

4**recovery of catechin and epicatechin from sago waste**

efflu- ent by adsorption onto activated carbon followed by supercritical CO2 desorption was demonstrated in this work. To study the ki- netic and equilibria of adsorption, synthetic aqueous catechin and epicatechin solution was used instead of sago waste effluent. The adsorption equilibria and kinetic were obtained isothermally at 303.15 K in static mode condition. The

37**adsorption equilibria of single and binary system**

were modeled using Langmuir and mod- ified extended Langmuir, respectively. It was found that both of

22**models could represent the** experimental **data well. In** adsorption kinetic experiments, **the**

well-known pseudo-first and pseudo-sec- ond models were employed to correlate the experimental data. The pseudo-second

9**model gave better representation of experimental data than the** pseudo-first **model.** The effect **of** initial concentration on **the**

value of fitting parameters k1 and k2 was also studied. The results indicate that k2 plays a role as time scaling factor, at high k2, shorter time is required to reach equilibrium. Adsorption using real sago waste effluent followed by supercrit- ical CO2 extraction indicates that this method has potential appli- cation in recovery catechin and epicatechin in industrial scale. Ethanol as co-solvent was required to obtain high recovery of cat- echin from the activated carbon. References [1] M.A. Soobrattee, V.S. Neergheen, A. Luximon-Ramma, O.I. Aruoma, T. Bahorun, Phenolics as potential antioxidant therapeutic agents: mechanism and actions, Mutat. Res. 579 (2005) 200–213. [2] L. Yu, K. Zhou, Antioxidant properties of bran extracts from ‘‘platte’’ wheat grown at different locations, Food Chem. 90 (2004) 311–316. [3] P. Vitaglione, A. Napolitano, V. Fogliano, Cereal dietary fibre: a natural functional ingredient to deliver phenolic compounds into the gut, Trends Food Sci. Technol. 19 (2008) 451–463. [4] A.R. Rechner, M.A. Smith, G. Kuhnle, G.R. Gibson, E.S. Debnam, S.K.S. Srai, K.P. Moore, C.A. Rice-Evans, Colonic metabolism of dietary polyphenols: influence of structure on microbial fermentation products, Free Radical Biol. Med. 36 (2004) 212–225. [5] A.R. Rechner, G. Kuhnle, P. Bremner, G.P. Hubbard, K.P. Moore, C.A. Rice-Evans, The metabolic fate of dietary polyphenols in humans, Free Radical Biol. Med. 33 (2002) 220–235. [6] O. Pourali, F.S. Asghari, H. Yoshida, Production of phenolic compounds from rice bran biomass under subcritical water conditions, Chem. Eng. J. 160 (2010) 259–266. [7] H. Epstein, Cosmeceuticals and polyphenols, Clin. Dermatol. 27 (2009) 475– 478. [8] S.M. Anthonysamy, N.B. Saari, K. Muhammad, F.A. Bakar, Browning of sago (Metroxylon sagu) pith slurry an influenced by holding time, pH and temperature, J. Food Biochem. 28 (2004) 91–99. [9] A.T. Pei-Lang, A.M.D. Mohamed, A.A. Karim, Sago starch and composition of associated components in palms of different growth stages, Carbohyd. Polym. 63 (2006) 283–286. [10] M. Ahmaruzzaman, Adsorption of phenolic compounds on low-cost adsorbents: a review, Adv. Colloid Interfaces 143 (2008) 48–67. [11] K. Baransi, Y. Dubowski, I. Sabbah, Synergetic effect between photocatalytic degradation and adsorption processes on the removal of phenolic compounds from olive mill wastewater, Water Res. 46 (2012). [12] A. Dabrowski, P. Podkoscielny, Z. Hubicki, M. Barczak, Adsorption of phenolic compounds by activated carbon – a critical review, Chemosphere 58 (2005) 1049–1070. [13] J. Qi, Y. Guo, H. Xu, Adsorption of phenolic compounds on micro- and mesoporous rice husk-based active carbons, Mater. Chem. Phys. 87 (2004) 96– 101. [14] C. Michailof, G.G. Stavropoulos, C. Panayiotou, Enhanced adsorption of phenolic compounds, commonly encountered in olive mill wastewaters, on olive husk derived activated carbons, Bioresour. Technol. 99 (2008) 6400– 6408. [15] M.L. Soto, A. Moure, H. Dominguez, J.C. Parajo, Recovery, concentration and purification of phenolic compounds by adsorption: a review, J. Food Eng. 105 (2011) 1–27. [16] F.E. Soetaredjo, A. Kurniawan, L.K. Ong, S. Ismadji, Incorporation of selectivity factor in modeling binary component adsorption isotherms for heavy metals-biomass system, Chem. Eng J. 219 (2013) 137–148. [17] C.H. Giles, D. Smith, A. Huitson, A general treatment and classification of the solute adsorption, I., Theor. J. Colloid Interface Sci. 47 (1974) 755–765. [18] C.H. Giles, A.P. D’Silva, I.A. Easton, A general treatment and classification of the solute adsorption isotherm, II, J. Colloid Interface Sci. 47 (1974) 766– 778. [19] 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. [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] 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. [22] K.K.H. Choy, J.F. Porter, G. McKay, Langmuir isotherm models applied to the multicomponent sorption of acid dyes from effluent onto activated carbon, J. Chem. Eng. Data 45 (2000) 575–584. [23] A. Kurniawan, H. Sutiono, N. Indraswati, S. Ismadji, Removal basic dyes in binary system by adsorption using rarasaponin–bentonite: revisited extended Langmuir model, Chem. Eng. J. 189–190 (2012) 264–274. [24] W. Plazinski, W. Rudzinski, A. Plazinska, Theoretical models of sorption kinetics including a surface reaction mechanism: a review, Adv. Colloid Interfaces 152 (2009) 2–13. [25] S. Lagergren, Zur

theorie der sogenannten adsorption geloster stoffe Kungliga Svenska Vetenskapsakademiens, Handlingar 24 (1898) 1–39. [26] G. Blanchard, M. Maunaye, G. Martin, Removal of heavy metals from waters by means of natural zeolites, Water Res. 18 (1984) 1501–1507. [27] A.N. Kosasih, J. Febrianto, J. Sunarso, Y.-H. Ju, N. Indraswati, S. Ismadji, Sequestering of Cu(II) from aqueous solution using cassava peel (Manihot esculenta), J. Hazard. Mater. 180 (2010) 366–374. [28] A. Kurniawan, H. Sutiono, Y.-H. Ju, F.E. Soetaredjo, A. Ayucitra, A. Yudha, S. Ismadji, Utilisation of rarasaponin natural surfactant for organo-bentonite preparation: application for methylene blue removal from aqueous effluent, Micropor. Mesopor. Mater. 142 (2011) 184–193. [29] A. Kurniawan, S. Ismadji, Potential utilization of Jatropha curcas L press cake residue as new precursor for activated carbon preparation: application in methylene blue removal from aqueous solution, J. Taiwan Inst. Chem. Eng. 42 (2011) 826–836. [30] F.E. Soetaredjo, S. Ismadji, Y.-H. Ju, Measurement and modeling of epicatechin solubility in supercritical carbon dioxide fluid, Fluid Phase Equilib. 340 (2013) 7–10. [31] F.E. Soetaredjo, S. Ismadji, M.J. Liauw, Y.-H. Ju, Catechin sublimation pressure and solubility in supercritical carbon dioxide, Fluid Phase Equilib. (2013). submitted for publication.

10**Author's personal copy Author's personal copy F.** E. Soetaredjo **et al.**

/ Chemical Engineering Journal 231 (2013) 406–413 407

10**Author's personal copy Author's personal copy F.** E. Soetaredjo **et al.**

/ Chemical Engineering Journal 231 (2013) 406–413 409

10**Author's personal copy Author's personal copy F.** E. Soetaredjo **et al.**

/ Chemical Engineering Journal 231 (2013) 406–413 411 Author's personal copy Author's personal copy F.E. Soetaredjo et al. / Chemical Engineering Journal 231 (2013) 406–413 413