# turnitin Turnitin Originality Report

Microporous and Mesoporous Materials 142 (2011) 184–19 by Suryadi Ismadji

From journal (Hippo-hippo)

Processed on 15-Feb-2018 17:48 WIB
ID: 916388542
Word Count: 5803

| Similarity Index | Similarity by Source | |
|---|---|---|
| 19% | Internet Sources: | 10% |
| | Publications: | 16% |
| | Student Papers: | 5% |

## sources:

**1** 1% match (publications)
Dadfarnia, S., A.M. Haji Shabani, S.E. Moradi, and S. Emami. "Methyl red removal from water by iron based metal-organic frameworks loaded onto iron oxide nanoparticle adsorbent", Applied Surface Science, 2015.

**2** 1% match (publications)
Sudaryanto, Y.. "High surface area activated carbon prepared from cassava peel by chemical activation", Bioresource Technology, 200603

**3** 1% match (Internet from 23-Sep-2017)
https://tel.archives-ouvertes.fr/tel-00817254/file/TH2010_Ravon_-_Ugo.pdf

**4** 1% match (Internet from 15-Feb-2010)
http://www.iau-jicr.com/pdf/Site2/JICR1(2)(2008)85.pdf

**5** 1% match (Internet from 03-Dec-2016)
http://polyhedron.dlut.edu.cn/pdf/37.pdf

**6** < 1% match (publications)
Sanghi, Rashmi, and Preeti Verma. "Decolorisation of aqueous dye solutions by low-cost adsorbents: a review", Coloration Technology, 2013.

**7** < 1% match (Internet from 29-Jun-2016)
http://electronicsandbooks.com/eab1/manual/Magazine/C/Chemical%20Engineering%20Journal/2009%20Volume%2
3/265-271.pdf

**8** < 1% match (publications)
Gercel, O.. "Preparation of activated carbon from a renewable bio-plant of Euphorbia rigida by H"2SO"4 activation and its adsorption behavior in aqueous solutions", Applied Surface Science, 20070330

**9** < 1% match (Internet from 28-Oct-2014)
http://www.textiletoday.com.bd/magazine/868

**10** < 1% match (publications)
Behnamfard, A.. "Equilibrium and kinetic studies on free cyanide adsorption from aqueous solution by activated carbon", Journal of Hazardous Materials, 20091015

**11** < 1% match (publications)
Madhumita Bhaumik, Rob I. McCrindle, Arjun Maity, Shilpi Agarwal, Vinod Kumar Gupta. "Polyaniline nanofibers as highly effective re-usable adsorbent for removal of reactive black 5 from aqueous solutions", Journal of Colloid and Interface Science, 2016

**12** < 1% match (publications)
Sajab, Mohd Shaiful, Chin Hua Chia, Sarani Zakaria, and Poi Sim Khiew. "Cationic and anionic modifications of oil palm empty fruit bunch fibers for the removal of dyes from aqueous solutions", Bioresource Technology, 2013.

**13** < 1% match (publications)
Wina, E.. "Saponins containing methanol extract of Sapindus rarak affect microbial fermentation, microbial activity and microbial community structure in vitro", Animal Feed Science and Technology, 20050609

**14** < 1% match (publications)
Wang, Weishan, Baicun Zheng, Weiguang Gong, Lefeng Fu, and Zhongjun Feng. "Interaction of polymethacrylate-g-PEO comb copolymers with natural bentonite in aqueous systems", Micro & Nano Letters, 2012.

**15** < 1% match (student papers from 27-Oct-2017)
Submitted to University of Leeds on 2017-10-27

**16** < 1% match (Internet from 22-Mar-2017)
http://www.kona.or.jp/jp/journal/pdf/2013.pdf

**17** < 1% match (Internet from 19-Jul-2014)
http://www.josunas.org/login/index.php/josunas/article/view/135

**18** < 1% match (publications)
V. Vadivelan, K. Vasanth Kumar. "Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk", Journal of Colloid and Interface Science, 2005

**19** < 1% match (publications)
Kushwaha, Atul Kumar, Neha Gupta, and M.C. Chattopadhyaya. "Enhanced adsorption of methylene blue on modified silica gel: equilibrium, kinetic, and thermodynamic studies", Desalination and Water Treatment, 2014.

**20** < 1% match (publications)
Plazinski, W.. "Theoretical models of sorption kinetics including a surface reaction mechanism: A review", Advances in Colloid and Interface Science, 20091130

**21** < 1% match (publications)
Mitra, Sayan, Lokendra Singh Thakur, Vineet Kumar Rathore, and Prasenjit Mondal. "Removal of Pb(II) and Cr(VI) by laterite soil from synthetic waste water: single and bi-component adsorption approach", Desalination and Water Treatment, 2015.

**22** < 1% match (publications)
Yue, Q.Y.. "Kinetics of adsorption of disperse dyes by polyepicholorohydrin-dimethylamine cationic polymer/bentonite", Separation and Purification Technology, 20070501

**23** < 1% match (publications)
Hameed, B.H.. "Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash", Chemical Engineering Journal, 20070915

**24** < 1% match (publications)
Zaghouane-Boudiaf, H.. "Kinetic analysis of 2,4,5-trichlorophenol adsorption onto acid-activated montmorillonite from aqueous solution", International Journal of Mineral Processing, 20110914

**25** < 1% match (publications)
Franca, A.S.. "Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds", Desalination, 20091130

**26** < 1% match (student papers from 27-Feb-2013)
Submitted to Malaviya National Institute of Technology on 2013-02-27

**27** < 1% match (publications)
Ugurlu, M.. "Adsorption of a textile dye onto activated sepiolite", Microporous and Mesoporous Materials, 20090301

**28** < 1% match (student papers from 01-Oct-2013)
Submitted to University of Johannsburg on 2013-10-01

**29** < 1% match (student papers from 12-Oct-2016)
Submitted to Savitribai Phule Pune University on 2016-10-12

**30** < 1% match (Internet from 27-Oct-2014)
http://www.freepatentsonline.com/6500992.html

**31** < 1% match (Internet from 06-Aug-2017)
https://www.ajol.info/index.php/sajc/article/download/123147/112687

**32** < 1% match (publications)
Hayati, Bagher, Mokhtar Arami, Afshin Maleki, and Elmira Pajootan. "Thermodynamic properties of dye removal from colored textile wastewater by poly(propylene imine) dendrimer", Desalination and Water Treatment, 2014.

**33** < 1% match (publications)
Gurses, A.. "The adsorption kinetics of the cationic dye, methylene blue, onto clay", Journal of Hazardous Materials, 20060417

**34** < 1% match (publications)
Wang, Qiu Ju, Rui Jiang Liu, Xiang Qian Shen, Ding Mei Wu, and He Hao Li. "Fabrication and Methyl Blue Adsorption Kinetics of α-$Fe_2O_3$ Nanotubes by Electrospinning", Advanced Materials Research, 2013.

**35** < 1% match (publications)
Liu, T.. "Adsorption of methylene blue from aqueous solution by graphene", Colloids and Surfaces B: Biointerfaces, 20120201

**36** < 1% match (publications)
Royer, B.. "Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions-Kinetic and equilibrium study", Journal of Hazardous Materials, 20090530

**37** < 1% match (student papers from 27-Oct-2017)
Submitted to University of Leeds on 2017-10-27

**38** < 1% match (Internet from 21-Nov-2017)
http://www.jmaterenvironsci.com/Document/vol9/vol9_N1/5-JMES-3408-El%20Alouani.pdf

**39** < 1% match (publications)
Ofomaja, A.E.. "Sorptive removal of Methylene blue from aqueous solution using palm kernel fibre: Effect of fibre dose", Biochemical Engineering Journal, 20080515

**40** < 1% match (publications)
A. El Sikaily. "Removal of Methylene Blue from aqueous solution by marine green alga Ulva lactuca", Chemistry and Ecology, 4/1/2006

**41** < 1% match (publications)
Cao, Chun-Yan, Li-Kai Meng, and Yong-Hua Zhao. "Adsorption of phenol from wastewater by organo-bentonite", Desalination and Water Treatment, 2014.

**42** < 1% match (student papers from 21-Dec-2016)
Submitted to International Islamic University Malaysia on 2016-12-21

**43** < 1% match (Internet from 13-Mar-2016)
https://dspace.aus.edu:8443/xmlui/bitstream/handle/11073/7663/35.232-2014.28%20Abdul%20Sami%20Gulistan.pdf?isAllowed=y&sequence=1

**44** < 1% match (Internet from 19-Apr-2016)
http://www.mdpi.com/1420-3049/21/4/405/htm

**45** < 1% match (publications)
Almasian, Arash, Mohammad Ebrahim Olya, and Niyaz Mohammad Mahmoodi. "Preparation and adsorption behavior of diethylenetriamine/polyacrylonitrile composite nanofibers for a direct dye removal", Fibers and Polymers, 2015.

**46** < 1% match (publications)
Li, Q.. "Two-step kinetic study on the adsorption and desorption of reactive dyes at cationic polymer/bentonite", Journal of Hazardous Materials, 20090615

**47** < 1% match (publications)
Ai, Lunhong, and Lili Li. "Efficient removal of organic dyes from aqueous solution with ecofriendly biomass-derived carbon@montmorillonite nanocomposites by one-step hydrothermal process", Chemical Engineering Journal, 2013.

**48** < 1% match (publications)

Li, B.. "Adsorption of simple aromatics from aqueous solutions on modified activated carbon fibers", Catalysis Today, 20101222

**49** < 1% match (Internet from 14-Mar-2014)
http://www.science.gov/topicpages/m/methylene+chloride+exposure.html

**50** < 1% match (Internet from 27-Jun-2017)
http://polen.itu.edu.tr/bitstream/11527/3777/1/3295.pdf

**51** < 1% match (publications)
Lei, Dai-Yin, Bo Li, Qiao Wang, Bo Wu, Lan Ma, and Heng Xu. "Removal of Neutral Red from aqueous solution using Pleurotus ostreatus nanoparticles by response surface methodology", Desalination and Water Treatment, 2015.

**52** < 1% match (publications)
Wołowicz, Anna, and Zbigniew Hubicki. "Sorption behaviour of Dowex PSR-2 and Dowex PSR-3 resins of different structures for metal(II) removal", Solvent Extraction and Ion Exchange, 2016.

**53** < 1% match (publications)
Feddal, I., A. Ramdani, S. Taleb, E.M. Gaigneaux, N. Batis, and N. Ghaffour. "Adsorption capacity of methylene blue, an organic pollutant, by montmorillonite clay", Desalination and Water Treatment, 2014.

**54** < 1% match (publications)
Atmani, F., A. Bensmaili, and A. Amrane. "Methyl orange removal from aqueous solutions by natural and treated skin almonds", Desalination and Water Treatment, 2010.

**55** < 1% match (publications)
Segal, S.R.. "Catalytic decomposition of alcohols, including ethanol, for in situ H"2 generation in a fuel stream using a layered double hydroxide-derived catalyst", Applied Catalysis A, General, 20030808

**56** < 1% match (publications)
A.M. Elfadly, I.F. Zeid, F.Z. Yehia, M.M. Abouelela, A.M. Rabie. "Production of aromatic hydrocarbons from catalytic pyrolysis of lignin over acid-activated bentonite clay", Fuel Processing Technology, 2017

**paper text:**

This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues. Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited. In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit: http://www.elsevier.com/copyright Microporous and Mesoporous Materials 142 (2011) 184–193

3**Contents lists available at ScienceDirect Microporous and Mesoporous Materials journal homepage: www.elsevier.com/locate/micromeso** Utilization

**of** rarasaponin natural surfactant **for**

organo-bentonite preparation: Application for methylene blue removal from aqueous effluent Alfin Kurniawan a, Hogiartha Sutiono a, Yi-Hsu Ju b, Felycia Edy Soetaredjo a, Aning Ayucitra a, Aditya Yudha a, Suryadi Ismadji a,⇑ a

2**Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia**

b

16**Department of Chemical Engineering, National Taiwan University of Science and Technology,**

43, Sec. 4 Keelung Rd., Taipei 106, Taiwan

5**article info Article history: Received** 26 May **2010 Received in revised form 24 November 2010 Accepted** 26 November **2010 Available online** 4 **December 2010 Keywords:**

Organo-bentonite Rarasaponin Adsorption abstract Rarasaponin that belongs to the natural surfactant was used as modifying agent for preparation of org- ano-bentonite. This surfactant was extracted from wild plant Sapindus rarak DC. The modifying process was conducted by microwave thermal irradiation. The characterization of bentonite and its modified form was carried out using FTIR, nitrogen sorption and XRD analysis. In order to test the adsorption capa- bility of organo-bentonite, batch adsorption experiments of methylene blue from aqueous solution using this adsorbent were conducted under several operating conditions. The highest adsorption capacity (qm) of organo-bentonite obtained in this study was 256 mg/g while for raw bentonite was 194

6**mg/g at 60 °C. The** adsorption isotherm and **kinetic data were**

modeled using several well known models.

10**Freundlich isotherm model** represented **the** adsorption **equilibrium data better than** the **Langmuir isotherm model.** For **the**

kinetic model, the pseudo-second order gave reasonable parameters and could correlate the kinetic data well. New mechanisms of organo-bentonite formation as well as adsorption of methylene blue on the surface of organo-bentonite were also proposed in this paper. Ó 2010 Elsevier Inc. All rights reserved. 1. Introduction Dyes, which are usually produced by synthetic process, are gen- erally characterized by complex aromatic molecular structure [1]. The presence of dyes in aqueous effluent such as in river stream can be noticed easily because dyes are colored and highly visible. The discharge of dyes directly into aqueous effluent can endanger living organism and its aquatic ecology because most dyes are toxic. Accumulation of dyes in water reduces the penetration of so- lar radiation into the body of water and harms the photosynthesis activity by plant and phytoplankton and subsequently significantly affects aquatic life and food web. Some dyes also possess carcino- genic and mutagenic properties which are very harmful to human life if accumulate in their body for a long time [2]. Several conventional methods for the treatment of wastewater containing dyes are available [3], and the most efficient one is the adsorption process, because it is simple in terms of operation and can remove the contaminant even at very low concentration. The success of an adsorption process completely depends on the cor- rect choice of the adsorbent, and the

22**most widely used adsorbent for** this purpose **is activated carbon. However,**

the main disadvan- tage of using activated carbon as the adsorbent is its high cost. ⇑

2**Corresponding author. Tel.: +62** 313891264; **fax: +62** 313891267. **E-mail address:**

suryadiismadji@yahoo.com (S. Ismadji).

3**1387-1811/$ - see front matter Ó** 2010 **Elsevier Inc. All rights reserved. doi:10.1016/j.micromeso.**

2010.11.032 Therefore, the use of activated carbon as adsorbent in large scale treatment of wastewater containing dyes is economically not fea- sible. In order to overcome this major drawback, a number of stud- ies for searching alternative adsorbents for wastewater treatment purpose have been conducted [4–7]. Modification of various kinds of clay and clay minerals using various kinds of chemical modifying agents for the removal of var- ious organic compounds from water or wastewater has been widely studied, and the results also had been summarized by sev- eral authors [8–10]. The use of chemicals for modification of clays and clay minerals often creates more serious problem to environ- ment and commonly needs expensive waste treatment system for unused or excess chemicals. Therefore, research on the utiliza- tion and modification of clays and clay minerals for wastewater treatment purpose (especially for dyes removal) should be directed towards the application of environmental friendly or natural chemicals as modifying agents. In this study we employed rarasa- ponin extracted from Sapindus rarak DC as a natural surfactant for bentonite modification.

54**To the best of our knowledge, there is no information**

available regarding the use of this natural surfactant as modifying agent for organo-bentonite preparation. Furthermore, the chemical reaction mechanism between rarasaponin and silanol group of bentonite during modification is presented in this paper. New adsorption mechanism between methylene blue and carbonyl group from organo-bentonite is also proposed. 2. Materials and methods 2.1. Chemicals

17**Methylene blue (basic blue 9, C.I. 52015; chemical formula** C16H18N3SCl **3H2O; MW, 373.90 g/mol) was** purchased **as**

analyti- cal-laboratory grade from Sigma–Aldrich and used without any further treatment. 2.2. Rarasaponin extraction Rarasaponin was extracted from dried fruits of wild plant S rar- ak DC. S rarak DC

13**is a tall tree which originated in South East Asia and is now widely distributed in Asia and Africa.** The **fruits**

were obtained from Klaten, Central Java, Indonesia. The extraction pro- cedure of rarasaponin from fruits of wild plant S rarak DC was car- ried out as follows: the dried fruits of S rarak DC were crushed by a micro-hammer mill (JANKE AND KUNKEL) and sieved in vibration screen (RETSCH) to obtain powder with particle size of 106– 150 Im. Twenty grams of S rarak DC

30**powder was added** to **200 mL of distilled water. The mixture was** then **heated at** 80 **°C**

for 60 min. The extract was then separated from the solid using centrifugation (Hettich Zentrifugen EBA-20) for 10 min at 4000 rpm. The supernatant was then concentrated by vacuum evaporation (BUCHI RE 121) and dried in a vacuum drying oven. The rarasaponin crystal were collected and crushed by using mi- cro-hammer mill, sieved using vibration screen (RETSCH) until its particle size was between 106–150 Im. 2.3. Organo-bentonite preparation Raw bentonite used in this study was obtained from mining site located in Pacitan, East Java, Indonesia. The cation exchange capac- ity (CEC) of bentonite was determined using ASTM C837-99 meth- od. The CEC value of the bentonite was 67.2 meq/100 g. The point of zero charge (pHpzc) of raw bentonite was 3.71. This value was determined by pH titration procedure [11]. The chemical element composition of raw bentonite used in this study was analyzed by atomic absorption spectrophotometer (AAS SHIMADZU AA6200) with flame emission. The results are summarized in Table 1. Prior to modification, bentonite was purified using hydrogen peroxide solution to remove any organic and inorganic impurities; raw bentonite was suspended in hydrogen peroxide solution for 18 h. After the purification was completed, the mixture was heated to remove excess hydrogen peroxide. Subsequently, the bentonite was repeatedly washed with distilled water, separated from solu- tion,

43**and dried in a** force circulation **oven at** 110 **°C for 24** h. **The** dried bentonite **was**

then crushed into powder. The preparation of organo-bentonite

53**was conducted using the following** procedure: **0.** 5 **g of** rarasaponin was dissolved **in** 25 **mL**

of distilled water. Subsequently, 5 g of bentonite powder was Table 1 Chemical element analysis result of raw bentonite. Element Percentage of mass fraction (w/w) Si 60.79 Al 20.84 Ca 4.77 Mg 1.21 Fe 0.31 Na 0.28 K 0.24 Mn 0.07

3**added to the solution. The mixture was** then **heated**

by microwave thermal irradiation (InexTron) for 90 s at 700 watt. The irradiation time above 90 s caused the destruction of bentonite as well as rara- saponin structure, while irradiation time below 90 s didn't allow the attachment of rarasaponin structure onto bentonite. The solid

41**was then separated from the** mixture, repeatedly **washed** using **distilled water, and dried at** 110 **°C**

for 24 h. 2.4. Characterization of raw bentonite and organo-bentonite The characterization of raw bentonite and its modified form was conducted using techniques such as FTIR, nitrogen sorption, and X-ray diffraction (XRD). The FTIR qualitative analysis was car- ried out in FTIR SHIMADZU 8400S using KBr method. The pore characteristic of bentonite and organo-bentonite was measured

2**by nitrogen adsorption at 196 °C**

in a Quadrasorb SI.

36**Prior to the** gas adsorption **measurements, the samples were degassed at 150** °C **in vacuum** condition **for**

2**24 h.** The **nitrogen adsorption–** desorption **isotherms were measured over relative pressure (P/** Po) **from approximately 10** 3 **to 0.** 998. **The**

pore size distribution of raw bentonite and organo-bentonite was determined by density functional theory (DFT) model in which the software available within the instrument, and medium regularization was used for the calculation. The

47**X-ray diffraction (XRD)** patterns **of powder were recorded on a Rigaku**

Miniflex Goniometer instrument at 30 kV and

55**15 mA, using** Cua **K radiation** at **a step size of 0.**

01°. 2.5. Adsorption studies The

1**adsorption process was conducted by adding a** known **amount of**

raw bentonite or organo-bentonite into 250 mL iodine flasks containing

33**100 mL of methylene blue solution** with **an initial concentration** of 500 **mg/L. The** solutions **were**

shaken in water- bath shaker (Memmert) at 100 rpm for 35 min at various temper- atures (30, 45, and 60 °C). After the process was completed, the flasks were then removed from the bath and the mixtures were centrifuged at 3500

38**rpm for** 5 **min to separate the** solution **from the** organo-bentonite. **The concentration of** methylene blue solution **was**

measured quantitatively with spectrophotometer (SHIMADZU UV/VIS-1700 PharmaSpec) at maximum wavelength (664.1 nm). The

18**amount of methylene blue adsorbed at**

equilib- rium was determined

37**by the following equation: qe ¼ ðC0 CeÞ V m ð1Þ where qe is**

the amount of methylene blue adsorbed at equilibrium (mg/g organo-bentonite),

4**C0 and Ce (mg/L) are the liquid phase** con- centrations **of** methylene blue **at initial and equilibrium,** respec- tively. **V is the volume of** methylene blue **solution (L) and** m **is the mass of** organo-bentonite **used (g).**

1**For kinetic study, the adsorption process was conducted by**

add- ing

31**a fixed amount of** organo-bentonite **(0.** 5 **g)** into **a series of 250 mL** iodine **flasks** that containing **100 mL**

methylene blue solu- tion at various

23**initial concentrations of 300,** 500, and 700 **mg/L.**

The flasks containing the

1**mixtures were** then **shaken in a temperature controlled water bath at a certain temperature. At** certain **time**

interval (every 5 min for the first 30 min, and subsequently the samples were analyzed every 1 min until 35 min), the concentra- tion of methylene blue

1**in the solution was measured** quantitatively **with spectrophotometer**

(SHIMADZU UV/VIS-1700 PharmaSpec).

29**The amount of** methylene blue **adsorbed at** a **time** interval **t (qt) was calculated using the equation** qt ¼ ðC0 CtÞ **V m**

ð2Þ Here qt

18**is the amount of methylene blue adsorbed at time** t **(mg/g** organo-bentonite), **and**

23**Ct (mg/L)** is **the liquid phase** concen- trations **of** methylene blue **at time** interval **t.**

3. Results and discussion 3.1. Rarasaponin Rarasaponin belongs to alkaloids group which has one or more oligosaccharide [12]. The FTIR spectra of rarasaponin and its func- tional group are given in Fig. 1 and Table 2, respectively. From Ta- ble 2, it can be seen that rarasaponin has functional groups such as hydroxyls, ester carbonyls, aromatic rings, and also alkanes group both in aliphatic and alicyclic structure. The absorption peak around 2345 cm 1 which belong to nitrile group may be due to impurities or some type of contaminants. 3.2. Characterization of bentonite and organo-bentonite FTIR absorption

14**spectra of bentonite and** its modified form **are** given **in Fig.** 2, while **the**

functional groups and its corresponding wave number values are summarized in Table 3. Fig. 2 and Table 3 reveal that the specific surface functional groups exist in raw bentonite and organo-bentonite. Table 3 indicates that the absorp- tion peak at 1257.23 cm 1 appears only in organo-bentonite spec- tra, this wave number

16**is assigned to the** asymmetrical **stretching** vibration **of C–O**

from carbonyl group from rarasaponin. The stretching vibration of C–O found in organo-bentonite indicates that carbonyl group from rarasaponin was intercalated into raw bentonite, leading to the formation of organo-bentonite. The nitrogen sorption isotherms of raw bentonite and its modified form are depicted in Fig. 3 Both raw bentonite and organo-bentonite possess mesoporous structure as

26**indicated by the presence of hysteresis** that lies **between adsorption and desorption isotherm** curve **at relative pressures above 0.**

5. The

22**BET surface area of raw bentonite and** organo **-bentonite**

are 92.3 Fig. 1. The FTIR absorption spectra of rarasaponin derived from Sapindus rarak DC. Table 2 Functional groups that contained in rarasaponin derived from Sapindus rarak DC. Functional groups

Wavenumber (1/cm) O–H stretch, free hydroxyl CH2 stretch bonded with hydroxyl group C–H stretch C@O stretch (ester carbonyls group) C–CH3 bend C–H bend bonded with hydroxyl group C–O stretch (carbonyls group) C@C stretch (aromatic rings group) 3538.17 3285.51 2931.6 1726.17 1441.69 1379.97 1248.82 1060.78 Fig. 2. The FTIR absorption spectra for raw bentonite and organo-bentonite. Table 3 The functional groups of raw bentonite and organo-bentonite. Functional groups Wanenumber (1/cm) Raw Organo-Bentonite bentonite O–H stretch for H2O in the silica matrix O–H stretch of silanol (Si–OH) groups O–H bend, for adsorbed H2O at bentonite interlayer C@O stretch of deacylated carbonyl group Si–O–Si stretch of the tetrahedral sheet Al–Al–OH bend Al–O–Si bend (for octahedral Al) Si–O–Si bend 3635.57 3279.73 1646.13 – 1027.88 920.95 697.22 437.81 3651.96 3231.51 1701.10 1257.23 1057.99 922.87 692.41 466.74

5**Fig. 3. Nitrogen adsorption–desorption isotherms of** raw bentonite **and**

organo- bentonite. and 84.6 m2/g, respectively. Total pore volume for raw bentonite is 0.61 cm3/g, while the organo-bentonite has higher pore volume (0.87 cm3/g). The higher pore volume of organo-bentonite than

46**that of raw bentonite** was **due to the intercalation of** rarasaponin molecules **into the**

structure of bentonie and causing the expansion of interlayer spacing of bentonite. The pore size distribution of raw bentonite and its modified form was determined by DFT (Density Functional Theory) analysis and the results are shown in Fig. 4. This figure clearly shows that both of these m0aterials have pore width that distribute mainly from 15 to 80 AÅ, which confirmed the mesoporous nature of both adsorbents. This result was in agree- ment with other previous works [13,14]. Physical characterization of layer structure for bentonite and organo-bentonite was conducted by X-ray diffraction. The XRD

56**Fig. 4. Pore size distribution of** raw **bentonite and** organo **-bentonite. Fig.**

5. XRD analysis results for raw bentonite and organo-bentonite. Fig. 6. The formation mechanism of organo-bentonite. results for raw

14**bentonite and organo-bentonite are shown in Fig.** 5. **The** diffraction peaks **of** both raw **bentonite and**

organo-bentonite appear at 9.44° and 8.22°, respectively. Other peaks are also ob- served in the angle range of 5–30°. The basal spacing (d001) of raw bentonite and organo-bentonite are 1.42 and 2.67 nm, respec- tively. The increase of basal spacing in organo-bentonite indicates that rarasaponin molecules were partially intercalated at bentonite interlayer spaces and expanded its interlamellar spacing and the later will promote methylene blue removal from aqueous solution. 3.3. Formation mechanism of organo-bentonite In this paper, the formation mechanism of organo-bentonite from bentonite and rarasaponin as a natural surfactant was pro- posed based on the following steps: the first step is the deacylation reaction of rarasaponin structure as indicated in Fig. 6. Rarasapo- nin, which belongs to biomacromolecules that contains two acyl groups (C2H3O+) attached in carbonyl structure. This acyl group at- tached to carbonyl structure will be deacylated when it is diluted in polar solvents such as water, natrium methoxide, or methanol as reported by Asao et al. [12]. This phenomenon will cause an imbalance negative charge on oxygen atom in both carbonyl sur- faces. This negatively charge of oxygen atoms in carbonyl groups will become the active binding sites for raw bentonite during the next step of reaction. The second step (Fig. 6b), the surface of silanol group (Si–OH) in tetrahedral sheet of bentonite will be protonated by the excess of H+ ions due to pHsolution > pHpzc [15]. The excess of H+ ions in solu- tion will penetrate into raw bentonite surface and then attack the hydroxyl groups in silanol, causing an imbalance positive charge on its surface. The successive of protonation in silicate layer of ben- tonite

24**can be readily followed by** the **changes in** characteristics of **absorption** spectra corresponded **to** vibration **of OH groups and octahedral** exchangeable **cations,** leading to **the**

formation of Si-rich phase in bentonite structure [16–18]. The protonation of silanol group in raw bentonite produce water molecules (H2O) with imbalance positive charge on its surface as indicated in step 2 in Fig. 6b. In the final step, the balancing of the negative charge Fig. 7. The proposed mechanism of methylene blue chemisorptions onto the surface of organo-bentonite. of oxygen atom in one side of deacylated carbonyl group with protonated silanol group (Si–OHþ2) in tetrahedral sheet of raw ben- tonite occurred leading to the formation of rarasaponin organo- bentonite as shown in Fig. 6c. 3.4. Chemisorption mechanism between methylene blue and organo- bentonite Rarasaponin organo-bentonite contains unoccupied side of deacylated carbonyl groups as indicated in Fig. 6. Methylene blue is a cationic dye and has positive charged surface generated from nitrogen center on its organic framework. Biprotonation form of this dye usually occurs at low pH or acid condition as illustrated in Fig. 7 [19]. The double positive charge of nitrogen center avail- able in methylene blue structure

45**plays an important role** during **the adsorption of this** dye in **the surface of**

organo-bentonite. The imbalance negative charge of oxygen atom in unoccupied deacylat- ed carbonyl group will be neutralized by immonium atom (N+) generated in the cyclohexene structure of methylene blue. 3.5.

12**Adsorption studies 3.** 5.1. **Effect of initial** solute **concentration The initial** solute **concentration provides** a necessary **driving force to overcome mass transfer** resistance **between the** liquid **and the solid**

phase [1]. The variation in initial solute concentration influences the amount of methylene blue adsorbed and its removal efficiency. Fig. 8 shows the effect of initial concentration of meth- Fig. 8. Effect of initial solute concentration to the amount of methylene blue uptake at various temperature. ylene blue on the amount uptake by raw bentonite and organo- bentonite. The increase of

1**initial solute concentration** caused **an in-** crease on **the amount of**

methylene blue adsorbed onto the raw bentonite and organo-bentonite surface. By increasing the initial concentration, the mass transfer resis- tance (kx) in the liquid phase becomes smaller because the mass transfer driving force (concentration gradient) in the solution be- comes greater, thereby providing faster adsorption rate of methy- lene blue (MB) onto both of the raw bentonite and organo- bentonite pore structure. 3.5.2.

35**Effect of temperature Temperature is one of the most important factors** in adsorption process. **The** effect **of**

temperature (30, 45, and 60 °C) as a function of time on the methylene blue adsorption is given in Fig. 9. Gener- ally,

7**temperature has two major effects on the adsorption** process. **Increasing the temperature** induces an **increase** in **the** diffusion **rate of adsorbate molecules**

onto adsorbent surface, thereby dimin- ishing mass transfer resistance in liquid phase as a result of the re- duced viscosity of bulk solution [1]. Increasing in temperature also enhances the equilibrium adsorption capacity for the particular adsorbate, especially if chemisorption is the control mechanism [1]. It is well known that organo-bentonite, which belongs to montmorillonite clay (MC), has a lattice with positive of thermal expansion coefficient, so that any temperature increase in the system will promote penetration process of adsorbate onto adsorbent surface layer [4,20]. Fig. 9. Effect of temperature as a function of time in methylene blue uptake at initial concentration of 70 mg/L. 3.5.3. Adsorption isotherm

8**Adsorption isotherm is the most important** part for illustrating **the mechanism of**

distributed adsorbate molecules between the li- quid phase and the solid phase at equilibrium state [1,4]. Equilib- rium adsorption isotherm is vital to the design in adsorption systems and provides valuable information in determining adsor- bent surface characteristics whether it is homogeneous or hetero- geneous [2]. In this study, adsorption isotherms data were correlated using two well known adsorption equations, Langmuir [21] and Freund- lich [22] models. Freundlich equation has the following form qe ¼ KFC1e=n ð3Þ

40**where qe is the amount of** MB uptake **per mass of adsorbent (mg/g),**

19**Kf and n are** both **Freundlich** temperature dependence **constants,** relating **to adsorption** affinity **(mg/g).(mg/L) n and adsorption intensity,** respectively. Greater value **of** n indicates that **the**

adsorp- tion isotherm becomes more nonlinear while if n close to 10, the adsorption process exhibits irreversible isotherm [23]. The Langmuir isotherm is also one of the most popular adsorp- tion models in illustrating adsorption phenomena. This model

7**has been successfully applied to many adsorption processes**

for liquid system [4,24,25]. This equation has the following form qe ¼ 1 KþLaCLeCe ð4Þ Here

1**qe is the amount of dye adsorbed** at equilibrium **per mass of adsorbent (mg/g), Ce is the** liquid phase **concentration** at equilib- rium **(mg/L),**

KL and aL are Langmuir equilibrium constants related Fig. 10. Experimental adsorption data at initial methylene blue concentration of 50 mg/L and the fit of Freundlich isotherm model. to the attraction of an adsorbate molecule onto an adsorbent sur- face (L/g) [23], and a constant that related to the net enthalpy of adsorption (L/mg) [4,26], respectively. The constant qm is equal to KL/aL (mg/g) and defined as the monolayer saturation capacity of adsorbent for particular adsorbate [4]. The essential characteris- tics

32**of the Langmuir isotherm** model **can be** also determined from **the dimensionless constant called equilibrium parameter, RL,** ex- pressed **by**

the following equation [14]: RL ¼ 1 ð5Þ 1 þ KLC0 The value of RL

15**indicate the** various **nature of adsorption** iso- therm **to be irreversible (RL = 0), favorable (0 < RL < 1), linear (RL** = 0), **or unfavorable (RL > 1).**

Figs. 10 and 11 show the adsorption equilibrium of methylene blue on rarasaponin organo-bentonite at various temperatures, and the fits using Freundlich and Langmuir models. In these fig- ures, the

48**experimental data are represented as symbols and** iso- therm fitting **as solid lines. The**

parameters for Freundlich and Langmuir were estimated using

6**non-linear least square method. The** optimal **parameters** from **the** fitting **of**

Freundlich and Lang- muir equations with experimental data are summarized in Tables 4 and 5, respectively. From Figs. 10 and 11, and Tables 4 and 5, it is clear that Freundlich model gave better representation for adsorption data. This evidence was confirmed by better coefficient value (R2) of Freundlich isotherm than Langmuir isotherm for both Fig. 11. Experimental adsorption data of methylene blue at initial concentration of 50 mg/L and the fit of Langmuir isotherm model. Table 4 The

8**Freundlich isotherm** parameter **for adsorption of methylene blue onto**

raw bentonite and organo-bentonite. T (°C) Raw bentonite Organo-bentonite Freundlich parameter Freundlich parameter

21**KF (mg/g).(mg/L) n n R2 KF (mg/g).(mg/L) n n R2** 30 5.4269 **1.**

8407 45 21.0227 2.9423 60 45.1755 4.4969 0.9919 9.2979 1.9469 0.9857 28.7116 2.6975 0.9924 68.7154 4.0515 0.9816 0.9730 0.9742 Table 5 The

8**Langmuir isotherm** parameter **for adsorption of methylene blue onto**

raw bentonite and organo-bentonite. T (°C) Parameter of Langmuir isotherm

50**KL (L/g) aL (L/mg) qm (mg/g) RL**

R2 Raw bentonite 30 1.1344 45 4.1802 60 26.5672 Organo-bentonite 30 1.8737 45 5.9551 60 27.9961 0.0065 175 0.0230 181 0.1372 194 0.0081 231 0.0241 247 0.1094 256 1.76 4.78 7.52 10 3 10 4 10 5 1.07 3.35 7.14 10 3 10 4 10 5 0.9895 0.9846 0.8798 0.9794 0.9549 0.8460 raw bentonite and organo-bentonite. Since the parameter KF in Freundlich equation cannot adequately represent the adsorption capacity of the adsorbent, therefore the adsorption capacity (mg/ g) of raw bentonite and organo-bentonite was determined based on Langmuir isotherm constant (qm).

27**It can be seen that the** max- imum **adsorption capacity of** organo-bentonite **was higher than** raw bentonite **at all temperatures.**

For comparison, the

25**Langmuir based maximum adsorption capacity of several** clay adsorbents **for**

methylene blue removal were also given in Table 6 [4,27–33]. 3.5.4. Adsorption kinetics Widely used equations such as Lagergren

11**pseudo-first order** [34] and **pseudo-second order** [35,36] **were used to** correlate our kinetic **experimental data.** The **Lagergren pseudo-first order**

has the mathematic expression as follows qe qeexpð k0tÞ ¼ qt ð6Þ and the

11**pseudo-second order can be written as:**

qt ¼ ksq2et=ð1 þ ksqetÞ ð7Þ where qe (mg/g)

9**and qt (mg/g) are the amount of** methylene blue **adsorbed at equilibrium** condition **and at time t (min), respectively.** k0 (min 1) **and** ks (g mg **1** min 1) are **the rate** con- stant for **pseudo-first order,**

and pseudo-second order kinetics, respectively. Table 6

25**Langmuir based maximum adsorption capacity of several** clay adsorbents **for** methylene blue removal. Clay adsorbent qm (mg/g clay) Reference Pacitan bentonite Organo-bentonite Montmorillonite clay Bentonite Clay Fibrous clay minerals Raw kaolin Spent activated clay Clay Perlite 175–194 Present study 231–256 Present study 289.12 Almeida et al. [4] 151–175 Hong et al. [27] 300 Bagane and Guiza [28] 85 Hajjaji et al. [29] 13.99 Ghosh and Bhattacharyya [30] 127.5 Weng and Pan [31] 6.3 Gurses et al. [32] 162.3 Dogan et al. [33] Fig. 12. The model fit of Lagergren pseudo-first order with kinetic experimental data at various

39**initial concentration of methylene blue. The**

plot of Lagergren pseudo-first order

28**with the experimental data is shown in Fig. 12.** From this figure **it can be seen that the**

34**pseudo-first order** describe **the experimental data** very **well. The pseudo-second order model** also can fit **the**

experimental data very well as indicated in Fig. 13. The

42**parameters of pseudo-first and pseudo-second order are** given **in Table** 7. **The**

parameter k0 in pseudo-first order is time scaling factor. Its value determines

52**how fast the equilibrium in the system can be reached**

[37]. This parameter

20**usually decreases with increasing** of **initial solute concentration in the bulk** liquid **phase**

[37–41]. Obvi- ously, the higher the initial concentration of solute in bulk liquid phase, the longer time is needed for that system to reach equilib- rium state [37]. The inconsistency of the parameter k0 is observed in this experiment as shown in Table 7. The parameters k0 increase with the increasing of initial solute concentration, hence the pseu- Fig. 13. The model fit of pseudo-second order with kinetic experimental data at various concentration of methylene blue. Table 7 Parameter constant of Lagergren pseudo-first and pseudo-second order for methylene blue uptake onto raw bentonite and organo-bentonite. Initial MB Pseudo-first order concentration k0 (min 1) qe (mg/g) R2 (mg/L)

44**Pseudo-second order** ks **(mg.g 1.min 1) qe** R 2 **(mg/g)**

Raw bentonite 300 0.4216 500 0.5257 700 0.5477 31.34 59.38 103.17 0.9957 0.0352 0.9987 0.0336 0.9993 0.0224 32.48 0.9995 60.61 0.9998 105.02 0.9999 Organo-bentonite 300 0.5136 500 0.5350 700 0.5460 67.05 98.61 137.57 0.9998 0.0314 0.9991 0.0218 0.9993 0.0167 68.32 0.9997 100.51 0.9998 140.06 0.9999 do-first order model is not the correct choice for representing the adsorption kinetic data of methylene blue onto raw bentonite and organo-bentonite. The parameter ks

20**of the pseudo-second order also**

strongly de- pend on the applied initial solute concentration. This parameter also is considered as a time scaling factor [37], therefore, this parameter will decrease with the increasing of initial concentra- tion. The parameter ks obtained from the fitting of our experimen- tal data is in agreement with theory. 4. Conclusion Rarasaponin extracted from fruit pericarp of S rarak DC was used as natural surfactant for organo-bentonite preparation. In order to test and compare the adsorption capability, both of raw bentonite and organo-bentonite

49**was used to remove methylene blue from aqueous solution.** New reaction mechanism **on**

the formation of organo-bentonite was proposed in this paper. The chemisorption

39**mechanism of methylene blue onto** organo-bentonite **was**

also gi- ven. The adsorption studies were conducted in batch system at dif- ferent operating condition.

10**Freundlich isotherm model** described **the** adsorption **equilibrium data better than** the **Langmuir isotherm model.** Based on **the**

Langmuir isotherm constant (qm), the highest adsorption capacity of organo-bentonite was 256 mg/g while for raw bentonite was 194

6**mg/g at 60 °C.** While for **the kinetic data,**

the

51**pseudo-second order** prevails over **the pseudo-first order model.** Acknowledgement **The** authors acknowledge **the**

funding of this work through Na- tional Taiwan University of Science and Technology-Widya Man- dala Surabaya Catholic University joint research project with contract no RP09-01 and Directorate General of Higher Education Republic of Indonesia through competitive grant for international publication with contract number 676/SP2H/PP/DP2M/VII/2009. References [1] M. Dogan, M. Alkan, O. Demirbaßs, Y. Özdemir, C. Özmetin, Chem. Eng. J. 124 (2006) 89–101. [2] M. Arami, N. Yousefi Limaee, N.M. Mahmoodi, Chemosphere 65 (2006) 1999– 2008. [3] T. Akar, T.A. Demir, I. Kiran, A. Ozcan, A.S. Ozcan, S. Tunali, J. Chem. Technol. Biotechnol. 81 (2006) 1100–1106. [4] C.A.P. Almeida, N.A. Debacher, A.J. Downs, L. Cottet,

C.A.D. Mello, J. Colloid Interf. Sci. 332 (2009) 46–53. [5] V.K. Gupta, I. Ali, V.K. Saini, T. Van Gerven, B.D. Van Bruggen, C. Vandecasteele, Ind. Eng. Chem. Res. 44 (2005) 3655–3664. [6] V.K. Gupta, I. Ali, V.K. Saini, J. Colloid Interf. Sci. 315 (2007) 87–93. [7] A.K. Jain, V.K. Gupta, A. Bhatnagar, N. Suhas, J. Hazard. Mater. 101 (2003) 31– 42. [8] S.P. Dubey, K. Gopal, J.L. Bersillon, J. Environ. Biol. 30 (2009) 327–332. [9] V.K. Gupta, N. Suhas, J. Environ. Manage. 90 (2009) 2313–2342. [10] P. Liu, L. Zhang, Sep. Purif. Technol. 58 (2007) 32–39. [11] J.J.M. Órfão, A.I.M. Silva, J.C.V. Pereira, S.A. Barata, I.M. Fonseca, P.C.C. Faria, M.F.R. Pereira, J. Colloid Interf. Sci. 296 (2006) 480–489. [12] Y. Asao, T. Morikawa, X.I.E. Yuanyuan, M. Okamoto, M. Hamao, H. Matsuda, O. Muraoka, D. Yuan, M. Yoshikawa, Chem. Pharma. Bull. 57 (2009) 198–203. [13] R. Koswojo, R.P. Utomo, Y.H. Ju, A. Ayucitra, F.E. Soetaredjo, J. Sunarso, S. Ismadji, Appl. Clay Sci. 48 (2010) 81–86. [14] E.K. Putra, R. Pranowo, J. Sunarso, N. Indraswati, S. Ismadji, Water Res. 43 (2009) 2419–2430. [15] S. Kubilay, R. Gurkan, A. Savran, T. Sahan, Adsorption 13 (2007) 41–51. [16] J. Madejová, J. Bujdák, M. Janek, P. Komadel, Spectrochim. Acta, Part A 54 (1998) 1397–1406. [17] P. Komadel, J. Madejová, J.W. Stucki, Appl. Clay Sci. 34 (2006) 88–94. [18] M.A. Vicente, Langmuir 12 (1996) 566–572. [19] Z. Khalid, Studies of the photochemical kinetics of methylene blue with reductants Department of Chemistry, University of Karachi, Karachi, 2001. [20] A.S. Ozcan, B. Erdem, A. Ozcan, Colloids Surf. A 266 (2005) 73–81. [21] I. Langmuir, J. Am. Chem. Soc. 38 (1916) 2221–2295. [22] H. Freundlich, Trans. Faraday Soc. 28 (1932) 195–201. [23] D.D. Do, Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, London, UK, 1998. [24] Z. Bouberka, A. Khenifi, N. Benderdouche, Z. Derriche, J. Hazard. Mater. 133 (2006) 154–161. [25] O. Hamdaoui, J. Hazard. Mater. 138 (2006) 293–303. [26] G. Rytwo, R. Huterer-Harari, S. Dultz, Y. Gonen, J. Therm. Anal. Calorim. 84 (2006) 225–231. [27] S. Hong, C. Wen, J. He, F. Gan, Y.S. Ho, J. Hazard. Mater. 167 (2009) 630–633. [28] M. Bagane, S. Guiza, Ann. Chim. 25 (2000) 615–626. [29] M. Hajjaji, A. Alami, A. El Bouadili, J. Hazard. Mater. B135 (2006) 188–192. [30] D. Ghosh, K.G. Bhattacharyya, Appl. Clay Sci. 20 (2002) 295–300. [31] C.H. Weng, Y.F. Pan, J. Hazard. Mater. 144 (2007) 355–362. [32] A. Gurses, S. Karaca, C. Dogar, R. Bayrak, M. Acikyildiz, M. Yalcin, J. Colloid Interf. Sci. 269 (2004) 310–314. [33] M. Dogan, M. Alkan, Y. Onager, Water Air Soil Pollut. 120 (2000) 229–248. [34] S. Lagergren, Kungliga Svenska Vetenskapsakademiens Handlingar 24 (1898) 1–39. [35] G. Blanchard, M. Maunaye, G. Martin, Water Res. 18 (1984) 1501–1507. [36] Y.S. Ho, J. Hazard. Mater. 136 (2006) 681–689. [37] W. Plazinski, W. Rudzinski, A. Plazinska, Adv. Colloid Interface Sci. 152 (2009) 2–13. [38] J. Febrianto, A.N. Kosasih, J. Sunarso, Y.H. Ju, N. Indraswati, S. Ismadji, J. Hazard. Mater. 162 (2009) 616–645. [39] S.J. Allen, Q. Gan, R. Matthews, P.A. Johnson, J. Colloid Interf. Sci. 286 (2005) 101–109. [40] G. Crini, Bioresour. Technol. 97 (2006) 1061–1085. [41] C. Namasivayam, D. Sangeetha, Desalination 219 (2008) 1–13. Author's personal copy Author's personal copy A. Kurniawan et al. / Microporous and Mesoporous Materials 142 (2011) 184–193 185 186 Author's personal copy A. Kurniawan et al. / Microporous and Mesoporous Materials 142 (2011) 184–193 Author's personal copy A. Kurniawan et al. / Microporous and Mesoporous Materials 142 (2011) 184–193 187 188 Author's personal copy A. Kurniawan et al. / Microporous and Mesoporous Materials 142 (2011) 184–193 Author's personal copy A. Kurniawan et al. / Microporous and Mesoporous Materials 142 (2011) 184–193 189 190 Author's personal copy A. Kurniawan et al. / Microporous and Mesoporous Materials 142 (2011) 184–193 Author's personal copy A. Kurniawan et al. / Microporous and Mesoporous Materials 142 (2011) 184–193 191 192 Author's personal copy A. Kurniawan et al. / Microporous and Mesoporous Materials 142 (2011) 184–193 Author's personal copy A. Kurniawan et al. / Microporous and Mesoporous Materials 142 (2011) 184–193 193