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40**basic dyes in binary system by adsorption using rarasaponin–bentonite: Revisited of extended Langmuir model**

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26**Nani Indraswati, Suryadi Ismadji ⁎ Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia**

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Adsorption Malachite green Methylene blue Binary system Extended Langmuir abstract The preparation of organo-bentonite via microwave radiation using natural surfactant (i.e. rarasaponin) from the tropical soapfruit pericarps of Sapindus rarak was conducted in this work. The adsorption per- formance of bentonite and its modified form was studied for the removal of two dyes (i.e. methylene blue and malachite green) in single and binary systems.

22**Langmuir and Freundlich models were applied to** evaluate **adsorption** equilibrium **data in single systems.**

3**From physical meaning interpretation of the model parameters, it was found that** Langmuir **model gave the best representation.**

A new approach in representing binary experimental isotherms with extended Langmuir model incorporating fractional surface coverage in 3D mesh plot was also verified. The results show that recently proposed modification of extended Langmuir model could be used to evaluate binary adsorption data well with reasonable fitted parameter value. © 2012 Elsevier B.V. All rights reserved.

23**1. Introduction The increasing environmental pollution from domestic and industrial effluents, particularly in the developing countries is of major concern.**

One kind of contaminants that are frequently pol- luting the water systems are dyes. Dyes are complex aromatic substances that indispensable in many industries such as tex- tile, paper, paint, leather, pigment, and pharmaceutical to impart color. Compared with natural dyes, synthetic dyes are superior in terms of color availability, permanent, ease to use, quick-setting and ensured by accurate formulas [1]. More than 100,000 kinds of synthetic dyes are commercially available with total amount of production reach 7 × 105 tonnes annually [2]. Of these, mala- chite green (MG) and methylene blue (MB) are two kinds of dyes that are most widely used among all other dyes in basic dye class [3,4]. Malachite green (4-[(4-dimethylaminophenyl)phenyl- methyl]-N,N-dimethylaniline) is a triphenylcarbenium salts, which composed of triarylmethane ring as the chromophore structure. Its applications are widely found in the paper, leather, silk and wool industries to color such products and aquaculture field as a biocide, fungicide and parasiticide therapeutic agent [3]. In other hand, methylene blue (3,7-bis(dimethylamino)phenothiazin-5- ium chloride) is a thiazine dye that used as redox indicator in the chemistry field, bacteria stain and indicator of viable yeast cell in the biology field and dyestuff for cotton, wool, paper and silk [4,5]. ∗

6**Corresponding author. Tel.: +62 313891264; fax: +62 313891267.**

24**E-mail address:** suryadiismadji **@yahoo.com (S.** Ismadji). 1385-8947/$ – **see front matter** © 2012 **Elsevier B.V. All rights reserved. doi:10.1016/j.**

cej.2012.02.070 Despite of the commercial importance of MG and MB dyes, the presence of these substances in natural environment (e.g. water bodies) even in trace quantities are highly undesirable for both toxicological and esthetical reasons. Moreover, the prolonged accu- mulation of these dyes in human body via food chain can cause several diseases and disorders due to their carcinogenic and muta- genic activity [6,7]. Therefore, the removal of these dyes from waste effluents is of interest prior to release into natural environment. Several conventional methods are available for the treatment and decontamination of dyes including physical, chemical and biological methods such as ozonation, photocatalysis, chemical oxidation, membrane filtration, flotation, coagulation, aerobic and anaerobic microbial degradation, enzyme degradation and adsorp- tion [8,9]. However, most of them are considered ineffective for handling colored effluents

16**due to chemical stability and low biodegradability of**

most dyes. In other hand, adsorption

16has proven to be a promising and cost effective method for

this purpose.

16Cost is actually an important parameter for the selection of the adsorbent materials

in designing adsorption system. In recent years, atten- tion has been focused on the search and development of various low cost alternative adsorbents for dyes removal, including agri- cultural solid wastes, industrial by-products and natural materials [10–12]. Clay has been emerged as potential natural adsorbents in the adsorption field due to their abundant reserve, low cost, high chem- ical and mechanical stabilities as well as high adsorptive properties. The applications of clay-based adsorbents for the removal of dyes have received growing attentions in the last decade [10,13–15]. Bentonite is a type of natural clay mineral that abundantly found in Table 1 Information on the methylene blue and malachite green dyes. Methylene blue (MB) Malachite green (MG) C.I number C.I name Chemical formula Molecular weight (g mol−1) (nm) Molecular 3D-structure 52015 Basic blue 9 C16H18N3SCl 319.85 664.1 42000 Basic green 4 C23H25N2Cl 364.91 617.3 many countries, including Indonesia. It is originated from the alter- ation of glass-rich volcanic rocks such as tuffs and ash deposits that composed of montmorillonite mineral as the main constituent [16]. The surface properties of bentonite can be remarkably enhanced by replacing inorganic metal cations (typically Na+ and Ca2+) at ben- tonite interlayer with organic cations. This substitution results in the hydrophobic surface nature of bentonite, which is suitable for the adsorption of organic substances. Several studies have reported on the modification of bentonite using various surfactants such as CTAB, CDBAC, CPC, and TMAB for dye removal [17–19]. However, the use of synthetic surfactants often causes environmental issues and need an extra cost for the treatment of unused chemicals. For this reason, the utilization of natural surfactant (i.e. rarasaponin) from the tropical soapfruit pericarps of Sapindus rarak is highlighted in this work. This work deals with the removal of two basic dyes (i.e. MB and MG) in single and binary systems using Trenggalek ben- tonite modified with rarasaponin surfactant. To date, there is no report on the removal of these dyes in binary system using rarasaponin–bentonite. A new approach of extended Langmuir model for representation of experimental isotherm in binary sys- tem was also proposed. Most of studies on the binary adsorption of various substances used such model to evaluate adsorption equilib- rium data by introducing original KL and qm parameters from single system [20–24]. However, such procedure cannot be precisely implemented in binary system, where the competition between adsorbate components for the adsorption sites occurs and may act as the sorption-controlling factor. Therefore, we proposed a revis- ited mathematic expression of qm and KL parameters in extended Langmuir model for binary system by inclusion of fractional surface coverage. 2. Materials and methods 2.1. Materials Malachite green (A.R. Grade, purity > 96%) and methylene blue (A.R. Grade, purity > 95%) were purchased from Sigma Aldrich and used as received. Some information about these dyes and their molecular structures are summarized in Table 1. Rarasaponin sur- factant used in this study was isolated from the tropical fruit pericarps of S. rarak by extraction process. The detail procedure of rarasaponin extraction can be found elsewhere [10]. 2.2. Preparation of adsorbents

19Bentonite used in this study was collected from the mining site located in Trenggalek, East Java, Indonesia. The type of bentonite from this location is Ca-bentonite. Prior to use, bentonite was puri- fied using H_2O_2 solution according to the procedure reported by Rahardjo et al. [25]. The

6**cation exchange capacity (CEC) of bentonite was** determined **based on the ASTM C837-99** standard **procedure**

and found to be 0.537 meq/g clay. The mineral compositions of ben- tonite were analyzed by atomic absorption spectrophotometry, in a FAAS Shimadzu AA6200 and the results are given as follows: SiO_2 57.8%, Al_2O_3 21.6%, Fe_2O_3 6.4%, CaO 4.3%, Na_2O 1.9%, MgO 1.5%, K_2O 0.7% and H_2O 5.8%. Rarasaponin–bentonite was synthesized by following proce- dure: 10 g of bentonite was dispersed into 50 mL distilled water containing rarasaponin surfactant with concentration

6**equivalent to 1.5 times of the CEC of** bentonite. **The**

mixture was then subjected to heating

6**in a microwave oven (National NN-S327 WF)** for 60 s **at**

heating power of 700 W. The resulting rarasaponin–bentonite

37**was then** repeatedly **washed with** distilled **water and dried in an oven at 100 ◦C for 24 h.**

2.3. Characterizations of adsorbents The pore structure of the adsorbents was analyzed by nitrogen adsorption at 77 K, in a Quadrasorb SI at relative pressure (p/p_0) range from approximately 0.001 to 0.995. The samples were degassed in vacuum condition at 423 K for at least 24 h prior to the adsorption analysis. The surface area of the adsorbents (S_{BET}) was determined by

33**standard BET equation applied** at **relative pressure range from 0.06 to 0.3. The total pore volume**

(V_T) of the adsorbents was calculated from the gas adsorption data at the highest relative pressure (p/p_0 = 0.995). The pore size distributions (PSDs) of the adsorbents were evaluated

14**by Density Functional Theory (DFT) model available within the instrument with medium regularization. The** layer structure **of** bentonite **and** rarasaponin–bentonite **was**

characterized by XRD method (Rigaku Miniflex Goniometer). The powder XRD patterns of the samples were collected at 30 kV and 15 mA, with a Ni-filtered CuK? radiation (= 1.542 Å) at a step size of 0.01◦. The surface functional groups of the adsorbents were analyzed by infrared spectroscopy, in a FTIR Shimadzu 8400S spectrometer using KBr disk pelleting technique. The

14**spectra data of the samples were recorded in** the mid-IR **wavenumber range**

(4000–500 cm−1). The pHpzc

32**(point of zero charge) of** bentonite **and** rarasaponin–bentonite **were determined by**

pH-drift procedure [26], and found to be 2.86 and 3.02, respectively. 2.4. Adsorption experiments For single systems, the stock solutions of dyes at initial concen- tration of 1000 mg/L (2.74 mmol/L – MG and 2.67 mmol/L – MB) were prepared by dissolving a known amount of dye into dis- tilled water. Adsorption isotherm experiments were carried out by adding various mass of adsorbent into a series of conical flasks con- taining 100 mL of dye solution. The flasks were then shaken in a Memmert shaking water bath at various temperatures (303.15 K, 323.15 K and 343.15 K) within 1–2 h until equilibrium condition reached. Subsequently, the mixture was centrifuged at 4500 rpm for 5 min to remove solid particles. The resultant

5**supernatant was taken and analyzed** its residual **concentration**

using a

5**Shimadzu UV/Vis-1700 spectrophotometer at maximum absorbance** wave- lengths ( ) **of**

617.3 nm for MG and 664.1 nm for MB,

5**respectively. The effect of pH was** also **studied at pH range of**

3–10.

5**To adjust the pH, an appropriate amount of 0.** 1 N **HCl or NaOH solutions was added to the system. The**

34**calibration curves for dyes** in single systems **were prepared by measuring the absorbance of different** concentrations **of the dyes. The** amount **of**

dye adsorbed at equilib- rium per unit of mass, qe, was calculated

9**as follows: qe (C0 − Ce) × V** = m (1) **where C0 and Ce are the initial and equilibrium concentrations of dye** in **solution** (mmol/L), **respectively, V is the volume of dye solution** (L) **and** m **is the mass of** the adsorbents **used (g).** For binary systems, **the dye** mixtures **were** prepared **by**

adding a known amount of MB dye (0.25 g, 0.5 g, 0.75 g and 1 g) into 1 L of MG

5**solutions with initial concentration of** 2.74 mmol **/L.**

Adsorption isotherm experiments were conducted based on the procedure in single system. The residual dye concentration in binary system was determined by measuring MG and MB dyes at 1 and 2, respectively,

20**to give optical densities of d1 and d2, as**

previously described by Choy et al. [20]: Ce,MG = kMG,M1kBM,2Bd,12 −− kkMMBG,,12k2MB,1 k d Ce,MB = kMGk,M1kGM,1Bd,22 −− kkMMGG,,22dk1MB,1 (2) (3) where kMG,1, kMG,2, kMB,1 and kMB,2

20**are the calibration constants for** MG **and** MB dyes **at the two wavelengths,** 1 **and** 2, **respectively. The** amount **of**

"i" dye adsorbed at equilibrium per unit of mass, qe,i, was calculated as follows: qe,i = (C0,i − Ce,i) ×

8**V m** (4) **where C0,** i **and Ce,** i **are the initial and equilibrium concentrations of** "i" **dye in the** mixture (mmol **/L),** respectively, **V is the volume** of dye mixture **(L) and m is the mass of** the adsorbents **used (g). 3. Results and discussion 3.1.** Pore **characteristics** of adsorbents **The**

pore structure of the solid is a critical variable in the adsorp- tion process since it determines the failure or success of such process from both equilibria and kinetic viewpoints. In this work, the pore structure of bentonite and rarasaponin–bentonite was analyzed by nitrogen adsorption at 77 K (Supporting information Fig. S1). From this figure, it can be confirmed the largely meso- porosity on the surface of bentonite and rarasaponin–bentonite, as denoted from the adsorption–desorption isotherm curves that exhibit type-IV shape based on IUPAC classification. Moreover, the mesoporous characters of the adsorbents were also observed from the hysteresis curve that lies

21**between adsorption and desorption isotherm** curves **at relative** pressure (p/p0) **above 0.**

5 (Supporting information Fig. S1). The surface area (SBET) of rarasaponin–bentonite was lower than bentonite (45.3 m2/g vs. 51.8 m2/g) while its total pore volume (VT) is higher than bentonite (0.49 cm3/g vs. 0.41 cm3/g). This is likely due to the formation of larger pore as a result of intercalation of organic modifier (i.e. acetyl cation) at the interlayer spacing of ben- tonite. Such pore characteristics are also evidenced from DFT result (Supporting information Fig. S2). 3.2. Layer characteristics of adsorbents

3**XRD analysis can be used as useful tool to characterize the layer structure of bentonite before and after modification. The powder XRD patterns of** bentonite **and**

rarasaponin–bentonite are shown in Fig. 1. From Fig. 1, it can be seen the reflection peak for Ca-bentonite at 2 = 5.92◦

3**with a d(0 0 1)-spacing value of** 14.93 **Å.**

The presence of other mineral compounds such as kaolin (K), quartz (Q) and calcite (Ca) in bentonite were also observed in the reflections relative to the planes K(0 0 1), Q(1 0 1) and Ca(1 0 4), respectively. After modification with rarasaponin surfactant, the reflection peak of rarasaponin–bentonite was shifted to lower angle of 2 = 5.77◦ with

39**an increase in d(0 0 1)-spacing**

value to 15.87 Å. The slightly

39**increase in** the **d(0 0 1)-spacing of**

rarasaponin–bentonite denotes that not all the interlayer sheets have been intercalated by acetyl cations. Such phenomena result in the expansion of the 2:1 interlamellar distance and later will promote the adsorption capacity of rarasaponin–bentonite for dyes removal. 3.3. Surface chemistry characteristics of adsorbents Infrared spectroscopy analysis (FT-IR) was performed to probe the conformation of surfactant cation species at the interlayer of rarasaponin–bentonite and identify the vibrational frequency changes of surface groups of the adsorbents, which are involved in the sorption process (figure not shown here). The FT-IR assignments of bentonite and rarasaponin–bentonite are summarized in Table 2. From Table 2, it can be seen the formation of rarasaponin–bentonite proceeded via ion exchange mechanism between inorganic inter- layer cation (i.e. Ca2+) and acetyl cation (C2H3O+), as indicated from the presence of C O stretch vibration at 1712 cm−1. Other FT-IR assignments in bentonite, which are the characteristics of montmorillonite clay also noticed such as

28**Al O Si** deformation **at 524 cm−1; Si O** stretch of quartz **at** 677 **cm−1; Al Al OH** defor- mation **at** 923 **cm−1;**

Si O stretch (in-plane) of tetrahedral sheet at 1040 cm−1; O H bend for adsorbed H2O at the interlayer of clay at 1638 cm−1 and O H stretch of aluminol (Al OH) or silanol (Si OH) at 3621 cm−1. The FTIR assignments of bentonite loaded with dyes (i.e. MB and MG) were also given in Table 2. From this table, it can be seen the presence of assignments of N O asymmetric stretch and S O stretch at 1528 cm−1 and 973 cm−1, respectively. These assignments may reveal to the binding of dye molecules onto the bentonite surface, which occur via electrostatic dipole–dipole

12**interaction between negatively charged oxygen** atoms **of the** deprotonated silanol sites **and positively charged** site **of the**

dye molecules (i.e. N+ for MG and S+ for MB). Moreover, the pres- ence of other assignment at 1592 cm−1, attributed to the aromatic C C stretch of the dye structure was also observed. The binding of the dye moieties in the silanol sites was also confirmed from the shifting of OH-stretch in the silanol species from 3621 cm−1 to 3563 cm−1 and reduction in its corresponding peak energy. Sim- ilar observations were also noticed in the FTIR assignments for rarasaponin–bentonite loaded with dyes. 3.4. Effect of pH The pH is regarded as a crucial parameter in the adsorption pro- cess since it may control the uptake mechanism of the adsorbate as well as influence the adsorption sites (e.g. the potential charge Table 2 FTIR assignments of pristine and dye-loaded adsorbents. FTIR assignments Wavenumber (cm−1) Bentonite rarasaponin–bentonite Bentonite + dyes Rarasaponin– bentonite + dyes O H stretch (Si OH or Al OH) C O stretch (C2H3O+) O H bend (adsorbed H2O at the interlayer of clay) C C stretch (aromatic ring) N O stretch (asymmetric stretch) Si O stretch (in-plane) for tetrahedral sheet S O stretch Al Al OH Si O stretch (quartz) Al O Si 3621 3614 – 1712 1638 1636 – – – – 1040 1017 – – 923 916 677 675 524 522 3563 – 1638 1592 1528 1025 973 916 690 523 3548 1706 1638 1581 1542 1032 968 916 682 524 of the site) on the solid surface. In the case of dye adsorption, the

10**changes in the structural and** colour **stabilities as well as degree of ionization for such adsorbate is also dependent on the pH of the solution** [27]. **The effect of pH on the adsorption of** MB **and** MG **dyes onto**

rarasaponin–bentonite in single system was studied at pH range of 3–10 and the results are given in Fig. 2. As noted in Fig. 2, a gradual increase in the percentage removal for both dyes was observed

4**in the pH range of 4–7 and** reached **its** maximum **at around pH 8.**

Increasing pH more than this value would lead to insignificant change in the percentage removal for both dyes. Moreover, a substantial reduction in the color inten- sity for MG was observed at pH > 9 while the color intensity of MB Fig. 1. Powder XRD patterns of bentonite (A) and rarasaponin–bentonite (B). Fig. 2. Effect of pH on the adsorption of dyes onto rarasaponin–bentonite (C0 = 2.74 mmol/L; t = 2 h; T = 303.15 K). slightly changes from pH 8 to pH 10. Therefore pH 8 was selected as optimum point and used for further experiments in this study. Since both MG and MB are cationic dyes, which have similar pH value for their highest removal, therefore pH 8 was also used during adsorption experiments in binary system. In basic solution, the adsorption of cationic dyes was favored due to the presence of negatively charged sites (i.e. deprotonated silanol) on the adsorbent surface, resulting in the electrostatic forces between these groups and positively charged dye molecules. As mentioned in previous paragraph, the pH of the solution also gives impact on the surface sites of the adsorbent, associated to the protonation and deprotonation of silanol groups (Si OH) as the active sites. The protonation and deprotonation of silanol species take place as follows:

> 21**Si OH + H+ → Si OH2+,** whenpHsolution < pHpzc **Si OH + OH− → Si O− + H2O,**

whenpHsolution > pHpzc In acidic solution (e.g. pH = 3), the adsorption of dyes was retarded due to sorption competition between hydrogen ions (H+) and dye molecules for occupancy of the active sites. Moreover,

> 4**high concentration of H+ ions causes** the **protonation of silanol groups,**

which resulted in ionic repulsion between cationic dye molecules and protonated silanol sites.

> 4**As the pH of the system increases, the** concentration **of H+ ions** in bulk solution **decreases and the silanol sites become deprotonated,** therefore **increasing the** neg- ative **charge density on the adsorbent surface and facilitating the adsorption of dye molecules.**

3.5. Adsorption isotherms Adsorption isotherm is the most valuable information in the adsorption studies for the practical and operational design of the sorption system since it describes the distribution of the adsorbate molecules within the solid and liquid phase at equilibrium. By evaluating this aspect, the information on the

> 41**adsorption kinetics of single component** system, **adsorption equilibria of** multicompo- nent **systems and adsorption kinetics of multicomponent systems**

can be obtained [28]. In the beginning, the adsorption models such as Langmuir, Freundlich, Sips, Toth, Dubinin–Raduskevich, Redlich–Peterson, Temkin, and Hill are extensively used to describe adsorption in gas phase, but in later, most of them can in prin- ciple be extended to liquid phase adsorption. Several studies have reported on the applications of different adsorption models to eval- uate various liquid phase adsorption systems [29–33]. 3.5.1. Adsorption isotherms for single system In this study, the two-well known adsorption models namely Langmuir and Freundlich were used to evaluate adsorption equi- librium data in single system. Langmuir model (1918) was proposed

> 27**based on** the **kinetic principle, that is the** adsorption **rate is equal to the** desorption **rate from the surface** to maintain zero **rate of**

accu- mulation when equilibrium is approached [28]. This model also assumed that the adsorption on surface occurs at a finite or defi- nite localized site

35**with no lateral interaction and steric hindrance between the adsorbed** species, **even on the adjacent sites** [34]. **The Langmuir**

model can be expressed mathematically as follows: qe = 1qm+KKLLCCee (5) where qm is the maximum adsorption capacity for the adsorbent, corresponds to the monolayer surface coverage (mmol/g) and KL

32**is Langmuir constant** represented **adsorption affinity (L/mmol). The**

characteristic of

25**Langmuir model can be** essentially **expressed by dimensionless constant** called equilibrium parameter, **RL, as** follows [35]: **RL = 1** + KLC0 **1** (6) **The** values **of RL** indicate various **nature of** the **adsorption**

systems

31**to be unfavorable (RL > 1), favorable (0 < RL < 1), linear (RL = 1) or irreversible (RL = 0). The**

second adsorption model used in this study was Freundlich. Freundlich (1932) proposed an adsorption on surface with non- ideal and reversible characteristics, which is not restricted to the monolayer adsorption [36]. To date,

15**this model has been** success- fully **applied to describe** various adsorption systems **of**

organics onto activated carbon and other adsorbents. However, the applica- tion of Freundlich model to evaluate adsorption data is generally valid in the narrow range of concentration since this model does not have Henry law limit

19**at low concentration and** saturation **limit at high-** end **concentration. The** Freundlich **model**

has the following form: qe = KF × Ce1/n (7) where KF and n are Freundlich constants for adsorptivity of solute [(mmol/g)(mmol/L)−n] and system heterogeneity, respectively. Higher value of n denotes the more heterogeneous the system is and the system approaches a rectangular isotherm (or irreversible isotherm) when n value is getting larger than about 10 [28]. The KF constant can also be regarded as the maximum adsorption capacity of the adsorbent only when the value of n approaches infinite [37]. The plots of the applied models against adsorption equilibrium data at various temperatures are depicted in Figs. 3 and 4.

The values of the model parameters were obtained by nonlinear least square fitting and the results are given in Table 3. From Figs. 3 and 4, it seems that both Langmuir and Freundlich models can fit all exper- imental data well, as indicated by good values of correlation factor (R2) that lies between 0.95 and 0.99. The values of KL and KF param- eters seem to increase at higher temperature, denoting that higher temperature favors the adsorption process due to greater adsorp- tivity of dye molecules toward the adsorbent surface. The increase in affinity parameter can also be explained from kinetics viewpoint that is higher temperature provides more energy for the solutes to undergo an interaction with the active sites on the solid surface. Similar observation is also noticed in the qm parameter, in which this value increases by the increase of temperature. Higher value of qm for rarasaponin–bentonite is likely due to the expansion of 2:1 interlamellar distance as a result of insertion of acetyl cation, which promotes the adsorption capacity of the adsorbent for dyes removal. Fitted parameters for the adsorption of MB and MG in single system at various temperatures. Adsorbent Adsorbate T (K) Langmuir parameters Freundlich parameters qm (mmol/g) KL (L/mmol) R2 RL KF (mmol.g−1) (mmol/L)−1/n n R2 Bentonite MG MB 303.15 323.15 343.15 303.15 323.15 343.15 0.51 0.53 0.56 0.54 0.57 0.59 1.56 2.13 3.23 1.67 2.46 3.34 0.98 0.97 0.99 0.98 0.97 0.97 0.19 0.15 0.10 0.18 0.13 0.10 0.31 0.35 0.41 0.34 0.37 0.42 2.73 3.00 3.39 2.72 3.15 3.22 0.98 0.98 0.99 0.97 0.97 0.98 Rarasaponin–Bentonite MG MB 303.15 323.15 343.15 303.15 323.15 343.15 0.66 0.87 0.93 0.71 0.89 0.96 1.71 2.31 3.66 1.75 2.54 4.13 0.98 0.98 0.97 0.99 0.98 0.98 0.18 0.14 0.09 0.18 0.13 0.08 0.36 0.47 0.73 0.41 0.49 0.76 2.15 2.34 2.72 2.19 2.27 2.81 0.98 0.97 0.95 0.98 0.98 0.94 By comparing the fitted parameters obtained, it is known

30**that the** adsorptivity **of MB dye** towards **the adsorbent** surface **is**

higher than MG dye. This result can be explained from molecular view- point that is small molecule gains

4**easier access to the internal pore-network of the adsorbent**

than large molecule. MB has lower molecular weight therefore its molecular size is smaller than MG. Moreover, higher affinity of MB dye is also caused due to more stabi- lized positive charge at the sulfur atom as a result of the −I inductive effect of the benzene ring [38], resulting in stronger dipole–dipole

12**interaction between negatively charged oxygen atom and** posi- tively **charged** sulfur **atom**

compared to

12**negatively charged oxygen atom and positively charged** nitrogen **atom. The**

value of n parameter in Freundlich model also increases with increase of temperature. This is due to faster mobility of the adsor- bate molecules in bulk solution, which rise the randomness degree of the system. The value of n parameter for rarasaponin–bentonite Fig. 3. Equilibrium plot and the models fit

13**for the adsorption of** MB **and** MG **in single system** onto bentonite **at** various temperatures. **Fig.**

4. Equilibrium plot and the models fit

13**for the adsorption of** MB **and** MG **in single system** onto rarasaponin–bentonite **at**

various temperatures. is considered to be higher than bentonite due to the present of organic modifier in the 2:1 interlayer space, causing the solid system to be more complex and heterogeneous. However, inconsistency results are noticed in this study that is the n values for rarasaponin–bentonite systems are lower than bentonite systems. This result reveals that Freundlich model fails to give best represen- tation from parameters justification. Therefore, its extended form (extended Freundlich) is not further

38**used to evaluate adsorption equilibrium data in** binary **system.**

3.5.2. Adsorption isotherms for binary system In this study, the extended Langmuir model was used to evalu- ate

38**adsorption equilibrium data** in **binary system. The** mathematic expression of **extended Langmuir**

model is given below: qe,i = 1 + m,iKj=L1,iKCLe,,iiCe,i q n (8) For binar∑y

13**system, the extended Langmuir equation above becomes:** qe **,1** = 1 + KLm **,1,** C1e,1L **,1+**

Ke,L1,2Ce,2 q K C (9) qe,2 = 1 + KLm,1,C2e,1L,2+ Ke,L2,2Ce,2 q K C (10) where qm and KL in Eqs. (9) and (10) are Langmuir constants for

6**maximum adsorption capacity of the** adsorbents **(mmol/g)** and adsorptivity of **the**

adsorbates (L/mmol) in single system, respec- tively. The applications of extended Langmuir model to represent adsorption equilibrium data in binary system have been reported in several studies [20–24]. From the previous studies, it was known that the evaluation of binary adsorption equilibrium data using extended Langmuir model was performed by inserting the values of qm and KL parameters in single system to calculate theoretical value of qe and compared it with experimental results. However, such procedure cannot be precisely implemented for binary adsorption system although it may give good correlation result. In binary sys- tem, the competitions (total or partial) between adsorbate species

22**for the adsorption sites on the** solid **surface** occur **and**

may act as the sorption-controlling factor. Such phenomena result in the cov- erage on the solid surface by both adsorbates with certain fractional loadings. Moreover, the adsorption potential on the surface is also affected by lateral interaction or competition between adsorbate species in the system. From the statements above, it is obvious that both KL and qm parameters from single Langmuir model cannot be adequately used to describe adsorption behaviors in binary system. Therefore, we proposed a revisited mathematic equation for qm and KL parameters for binary adsorption system as follows: qm(bin) = qm,1(sin) 1 + qm,2(sin) 2 (11) KL,1(bin) = KL,1(sin) exp (− 2 1) (12) KL,2(bin) = KL,2(sin) exp (− 1 2) (13) Fig. 5. Comparison plotting between original-extended Langmuir (A and B) and proposed-extended Langmuir (C) models against binary experimental data (2.74 mmol/L MG + 1.34 mmol/L MB – bentonite – 303.15 K). where 1 and 2 are constants representing fractional loading of each adsorbate species on the adsorbent surface. The mathematic relationship between qm and is clearly understand that is the sur- face of the adsorbent was occupied by both adsorbates with certain loadings. In other hand, the mathematic relationship between KL and can be explained principally from the surface coverage view- point that is the adsorption potential on the surface is weakened when the adsorbate species competed each other for the adsorp- tion sites. Since the competition between adsorbate species occurs in binary system, therefore the values of adsorption potential (or affinity) for each adsorbate should be lower than in single system. Substitute Eqs. (11)–(13) into extended Langmuir model give: qe,1(bin) = 1 + K(Lq,1m(s,i1n()sienx)p1(−+ q2m/,21(s)iCn)e,12()bKinL),1+(siKn)L,e2x(spin()−exp(−1)1C/e,12(b)iCne),2(bin) 2 / qe,2(bin) 1 + KL,1(sin) exp(− 2/ 1)Ce,1(bin) + KL,2(sin) exp(− 1/ 2)Ce,2(bin) = (qm,1(sin) 1 + qm,2(sin) 2)KL,2(sin) exp(− 1/ 2)Ce,2(bin) (14) (15) Fig. 6. Model fit of proposed-extended Langmuir at different viewpoints against binary adsorption data (2.74 mmol/L MG + 1.34 mmol/L MB – bentonite – 303.15 K). Fig. 7. Model fit of proposed-extended Langmuir at different viewpoints against binary adsorption data (2.74 mmol/L MG + 1.34 mmol/L MB – rarasaponin–bentonite – 303.15 K). Both equations above will return to single Langmuir model if only one adsorbate species is presented in solution (i.e. 2 = 0 in Eq. (14) and 1 = 0 in Eq. (15)). To get better understanding whether our model is applicable to represent binary adsorption experi- mental data, we compare the plot of experimental isotherm data (2.74 mmol/L MG + 1.34 mmol/L MB – bentonite – 303.15 K) against original-extended Langmuir (Eqs. (9) and (10)) and proposed- extended Langmuir models (Eqs. (14) and (15)) in 3D mesh plot, as presented in Fig. 5. In Fig. 5, the blank data points represent the plot of Ce,MB as x- axis vs. Ce,MG as y-axis vs. qe,MB as z-axis while the filled data points denote the plot of Ce,MG as x-axis vs. Ce,MB as y-axis vs. qe,MG as z- axis. For binary system, the plot of the model should fit both data points since the concentration of both adsorbate species in bulk solution is in a dynamic balance with the interface concentration at equilibrium condition. Fig. 5A clearly shows a very poor fit between the mesh plot and experimental data points since all data points lie below the mesh plot. This result may confirm that evaluation of binary adsorption data by comparing theoretical value of qe with experimental results is not valid. In other hand, Fig. 5B and C denote a very good fitting between the models and experimental data. However, the values of fitted parameters obtained from original- extended Langmuir model (Fig. 5B) are deviate away as those for single system therefore this fitting is not valid from parameters interpretation viewpoint. To this end, the value of fitted parameter obtained (1) from proposed-extended Langmuir model (Fig. 5C) is reasonable with good correlation factor (R2 = 0.95), therefore this proposed model is further used for evaluation of binary adsorption equilibrium data in this study. The plotting of Eqs. (14) and (15) against binary experimen- tal data (e.g. 2

2**.74 mmol/L MG + 1.** 34 **mmol/L**

MB and 2

2**.74 mmol/L MG + 1.** 34 **mmol/L**

MB) onto bentonite and rarasaponin–bentonite at 303.15 K was performed by SigmaPlot software and the results are displayed in 3D-mesh plot (Figs. 6 and 7). The fitted parameter (1) was obtained by nonlinear least square fitting and the results are summarized in Table 4. The

18**values of qm(bin), KL,1(bin) and KL,2(bin)** parameters **are**

calculated by inserting the value of 1 parameter into Eq. (11), Eq. (12) and Eq. (13), respectively.

30**From Table** 4, **it can be seen the value of**

1, which refers to the fractional surface coverage by MG, decreases as the concentration of MB in the dye mixture increases. At the same concentration (i.e. 2.74 mmol/L (1000 mg/L) MG + 2.67 mmol/L (1000 mg/L) MB), the fractional loading of MB (2) is larger than MG, denoting that MB is preferentially adsorbed on the adsorbent surface than MG.

18**This result** is **consistent with adsorption characteristics in single system that** is **the** adsorptivity **of** MB is larger **than**

MG, causing more cov- erage on the adsorbent surface. Increasing temperature also leads to the increase in affinity constants for both dyes, denoting that higher temperature favors the adsorption process. Higher value of qm for rarasaponin–bentonite is due to larger interlamellar spaces so that more dye molecules can occupy the internal pore in the solid matrix. Fitted and calculated parameters for MB and MG adsorption in binary system at various dye mixtures and temperatures. Adsorbent Dye mixture T (K) Fitted parame- ter 1 Calculated parameters R2 2 KL,1(bin) KL,2(bin) qm(bin) Bentonite Rarasaponin–bentonite 2

2**.74 mmol/L MG** + 0.67 **mmol/L** MB 2.74 **mmol/L**

MG + 1.34 mmol/L MB 2.74

2**mmol/L** MG + **2.** 01 **mmol/L** MB 2 **.74 mmol/L MG** + 2.67 **mmol/L** MB 2.74 **mmol/L**

MG + 0.67 mmol/L MB

112.74 mmol/L MG + 1.34 mmol/L

MB 2.74

2mmol/L MG + 2. 01 mmol/L MB 2 .74 mmol/L MG + 2.67 mmol/L MB 2.74 mmol/L

MG + 0.67 mmol/L MB

112.74 mmol/L MG + 1.34 mmol/L

MB 2.74

2mmol/L MG + 2. 01 mmol/L MB 2 .74 mmol/L MG + 2.67 mmol/L MB 2.74 mmol/L

MG + 0.67 mmol/L MB

112.74 mmol/L MG + 1.34 mmol/L

MB 2.74

2mmol/L MG + 2. 01 mmol/L MB 2 .74 mmol/L MG + 2.67 mmol/L MB 2.74 mmol/L

MG + 0.67 mmol/L MB

112.74 mmol/L MG + 1.34 mmol/L

MB 2.74

2mmol/L MG + 2. 01 mmol/L MB 2 .74 mmol/L MG + 2.67 mmol/L MB 2.74 mmol/L

MG + 0.67 mmol/L MB

11**2.74 mmol/L** MG + 1.34 **mmol/L**

MB 2.74 mmol/L MG + 2.01 mmol/L MB 2.74 mmol/L MG + 2.67 mmol/L MB 303.15 0.57 0.51 0.42 0.36 323.15 0.55 0.49 0.38 0.33 343.15 0.51 0.45 0.34 0.31 303.15 0.53 0.46 0.38 0.32 323.15 0.49 0.44 0.35 0.30 343.15 0.47 0.41 0.31 0.27 0.43 0.74 0.49 0.60 0.58 0.39 0.64 0.26 0.45 0.94 0.51 0.75 0.62 0.42 0.67 0.28 0.49 1.24 0.55 0.95 0.66 0.46 0.69 0.35 0.47 0.70 0.54 0.53 0.62 0.34 0.68 0.20 0.51 0.82 0.56 0.65 0.65 0.36 0.70 0.22 0.53 1.19 0.59 0.87 0.69 0.40 0.73 0.25 0.44 0.59 0.81 0.95 0.73 0.94 1.15 1.30 1.18 1.47 1.99 2.13 0.57 0.75 0.95 1.09 0.97 1.16 1.48 1.66 1.70 2.06 2.64 2.85 0.51 0.51 0.52 0.52 0.53 0.54 0.54 0.54 0.56 0.57 0.57 0.57 0.66 0.66 0.67 0.67 0.87 0.87 0.88 0.88 0.96 0.97 0.97 0.97 0.88 0.95 0.94 0.91 0.91 0.89 0.88 0.93 0.92 0.91 0.93 0.94 0.95 0.91 0.89 0.91 0.94 0.93 0.91 0.95 0.89 0.92 0.94 0.91 4. Conclusions Preparation of rarasaponin–bentonite via microwave radiation has been demonstrated in this work. Batch adsorption experi- ments at three different temperatures were performed to test adsorption performance of bentonite and rarasaponin–bentonite for the removal of methylene blue and malachite green in sin- gle and binary systems. Experimental isotherms in single systems

3**were analyzed by Langmuir and Freundlich models and their** fit- ting **results were contrasted. From physical meaning interpretation of the model parameters, it was found that** Langmuir **model gave the best representation.**

For binary system, experimental isotherms were presented in the 3D mesh plot and were interpreted using extended Langmuir model incorporating fractional surface cover- age ( ). The results show that recently proposed modification of extended Langmuir model can be used to describe binary adsorp- tion experimental data well with reasonable fitted parameter value.

17**Appendix A. Supplementary data Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2012.02.**

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36**et al. / Chemical Engineering Journal** 189–190 **(2012)** 264–274 **Table 3**

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7**Chemical Engineering Journal 189–190 (2012)**

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7**Chemical Engineering Journal 189–190 (2012)**

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36**et al. / Chemical Engineering Journal** 189–190 **(2012)** 264–274 **Table 4**

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7**Chemical Engineering Journal 189–190 (2012)**

264–274 273 274 Author's personal copy A. Kurniawan et al. / Chemical Engineering Journal 189–190 (2012) 264–274