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N-methylated diaminotriphenilmethane dye (malachite green) on natural rarasaponin modified kaolin Anita Carolina Suwandi,

27**Nani Indraswati & Suryadi Ismadji** a a **Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya, 60114, Indonesia** Phone: **Tel. +62** 31 3891264 **Fax:**

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664738 Adsorption of N-methylated diaminotriphenilmethane dye (malachite green) on natural rarasaponin modified kaolin Anita Carolina Suwandi, Nani Indraswati, Suryadi Ismadji*

10**Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia Tel. +62 31 3891264; Fax: +62 31 3891267;** email: suryadi **@mail.**

wima.ac.id Received 24 November 2011; Accepted 22 January 2012 ABSTRACT The modification of kaolin using natural surfactant rarasaponin was studied. The effective- ness of kaolin and rarasaponin-kaolin was evaluated for removal of malachite green (MG) from the aqueous solution. The temperature dependent forms of

12**Langmuir, Freundlich, Sips and Toth** model **were** employed **to correlate the** adsorption experimental **data.**

Even all iso- therms used in this study, visually can correlate the experimental data well, however Sips model gave consistent and reasonable values of the fitted parameters. Kinetic data were ana- lyzed using pseudo-first- and pseudo-second-order, and pseudo-first-order gave reasonable values of fitted parameters. Thermodynamic properties of adsorption of MG onto kaolin and rarasaponin-kaolin were also obtained in this study. Keywords: Adsorption; Modification; Kaolin; Rarasaponin-kaolin 1. Introduction Synthetic dyes have been widely used in many industrial processes. Some kinds of these dyes are safe and can be used for food colouring others are very toxic for human and even for the environment. Cur- rently, synthetic dyes in industrial processes almost replace natural dyes due to its cheaper price, brighter colour and better properties to the dyed materials. Many of these dyes are dangerous and must be removed before getting discharged to environment. Even at very low concentration, the presence of dye in water could be highly toxic to aquatic systems [1]. Also, the presence of dye in water may influence aquatic ecosystem which is due to

41**acute and/or chronic effects on** the **exposed organisms, depending on the exposure time and dye concentration,**

or by *Corresponding author.

44**blocking the passage of light through the water** so it can **interfere with the** growth **of** microorganisms **and hinder photosynthesis in**

aquatic plants [2–4]. Several dyes

4**cannot be** removed **completely by conventional biological treatment processes, such as activated sludge and anaerobic digestion,**

since they are also

4**resistant to light and moderate oxidative agents**

[5]. Basic Green 4 (BG 4) or malachite green (MG) is a cationic dye that belongs to N-methylated diaminotriphenylmethane dye and most

43**widely used for** colouring **purpose among all other dyes of its** cate- gory [3]. **This dye is** used **as** biocide **in the**

aquacul- ture industries. It is also used as colouring agent in leather, wool, jute, paper, cotton, silk and acrylic industries as well as

18**food coloring agent, food addi- tive, medical disinfectant and anthelminthic**

[3,6,7]. However, MG is hazardous, carcinogenic and acts as a liver promoter [8]. It

18**causes damage to liver,** kidney, **spleen and heart;**

decreases growth, food intake and fertility rates; inflicts lesions on eyes, skin, lungs and bones [9]. MG easily reduces the tissue of fish and mice to persistable leuco-MG, which acts as a tumor promoter [10,11]. Several studies also reveal that the degradation products of MG have carcinogenic poten- tial [9,12]. However, despite a lot of

22**data on its toxic effects, MG is still used in aquaculture and** many **other industries** [3,13–16]. **Therefore, the removal of** BG 4 **from** effluents **is very** essential to protect **the**

water resources [9]. Several commonly used methods for the removal dyes from wastewater are adsorption, nanofiltration, electrocoagulation, 32**coagulation and precipitation, chemical oxidation, electrochemical oxidation, photo- oxidation,** colloidal gas aphrons, **ozonation, supported liquid membrane and liquid–liquid extraction** [15,17]. **The**

advantages and disadvantages of each method have

9**been reviewed in several papers** [17–24]. **Among** these **mentioned methods, adsorption** process **are** more **attractive due to their high efficiency, low-cost,** very simple design, **availability and easy**

for

9**recovery and reuse of adsorbent** [5,19]. Moreover, **adsorption**

can

15**remove toxic chemicals without** lowering **the quality of water or leaving any** hazardous **degraded products**

15**in comparison to biochemical,** electrochemi- cal **or photochemical degradation processes**

[25]. Granular

24**activated carbon** (GAC) **is the most widely used adsorbent**

[26]. Activated carbon adsorp- tion

4**shows high effectiveness in removal of organic and inorganic pollutants, including dyes and** pig- ments. **However, the use of this adsorbent in** waste- water **treatment is still limited because of its high cost and difficulty in regeneration.**

This fact triggers research and development for another low-cost adsor- bents, such as clay [16,27–30], bagasse [31], chestnut shell [32], banana peel [33,34], chitosan [35,36] and many more. Clay has been used for different kinds of applica- tion [37,38], and one of the application is in adsorp- tion area. One of the most commonly used clay as low-cost adsorbent is kaolin with $Al2Si2O5(OH)4$ or $Al2O3$ $2SiO2$ $2H2O$ chemical structure that belongs to the natural alumino silicate clay adsorbents. Kaolinite clay has been studied as an adsorbent for removal of heavy metal ions and organic contaminants from aqueous medium [39]. The chemical composition of kaolinite,

23**$SiO2$: 40 mol%, $Al2O3$: 20 mol% and $H2O$:40 mol%.** Kaolin crystal structure **is**

composed of

39**a two-layer triclinic structure, consisting of stacked pairs of tetrahedral silica sheets and octahedral** alu- mina **sheets. The**

oxygen atoms hold each pair of sheets together,

9**while successive pairs are** bound **by hydrogen bonding between silica–oxygen and** alu- minumhydroxyl **groups.**

5**The surfaces of kaolinite are** predicted **to** have **a constant structural negative charge, due to the isomorphous substitution of Si4+ by Al3+ in the silica layer,** while **the charge on the alumina face and on the edges** is caused by **the** pro- tonation **/deprotonation of exposed hydroxyl groups** which **depends on the pH** value **of the solution**

[40,41]. There are large quantities of kaolin in Indone- sia because it is one of abundant natural resources, therefore it may be used as an alternative adsorbent due to its stability in water, low cost and potential adsorption application. Unfortunately, kaolinite has a low-cation exchange capacity (CEC), and therefore it is not expected to be an ion exchanger of high order [39,42]. Cationic sur- factants have been studied to increase the adsorption capacity of clay for hydrophobic organic contaminants (HOCs) [43]. Therefore, modification using cationic surfactant is necessary to improve kaolin adsorption capacity. The modified kaolin is called organo-kaolin, related to addition of organic compound into the kaolin. Commonly used surfactants act as modifying agent that are synthetic surfactants, such as cetyltri- methylammonium bromide (CTMAB) [44], octadecylt- rimethylammonium bromide (ODTMA) [30], N-[3-[(trimethoxysilyl)propyl]diethylenetriamine (MPDET) [45]. These surfactants may have non-biodegradable properties due to its synthetic origin, which may cause environmental problems. For minimizing the problem, ecological friendly natural surfactant was used as modifying agent in this study. Lerak (Sapindus rarak DC) is easily found in Indo- nesia, especially in Java. S. rarak DC contains natural surfactant called as rarasaponin, which belongs to sugar derivatives compound that may be found in plants, which is characterized by forming foam when dissolved in water. Rarasaponin has complex chemi- cal structure; different chemical structures of rarasa- ponin can be found elsewhere [46]. The most widely used method to obtain rarasaponin is solid–liquid extraction (leaching). Different kind of solvents can be used to extract rarasaponin from its solid matrices such as water (H2O), methanol (MeOH), ethanol (EtOH) and sodium methoxyde (NaOMe) [46]. Since rarasaponin is a natural surfactant, therefore it has great potential application as an environmental friendly chemical for modification of kaolin for dye removal. To the best of our knowledge, currently there is no information about utilization of rarasaponin as surfac- tant for organo-kaolin preparation; therefore, this is the novelty of our study. In order to test the adsorp- tion capability of rarasaponin-kaolin, the

35**adsorption experiments of MG from aqueous solution** were con- ducted **in batch**

mode in several temperatures. The adsorption isotherms of MG onto natural kaolin and rarasaponin-kaolin were correlated using temperature dependent forms of Langmuir, Freundlich, Sips and Toth models. The kinetic data were correlated by well known pseudo-first- and pseudo-second-order models.

36**2. Materials and methods 2.1. Materials** Kaolin **used in this study was obtained from** Pacit- an, **East Java, Indonesia. The** kaolin was crushed and sieved using the ASTM standard sieves to obtain 180– 200 mesh particle size. MG, also known as BG 4, was used as adsorbate. MG is a cationic N-methylated diaminotriphenylmethane dye, contains –N(CH3)2 functional group, C.I. 42000 (certified number for MG), chemical formula = C23H25N2Cl, FW (formula weight or molecular weight) = 364.7 and kmax = 616.4 nm. MG

25**was purchased from Sigma Aldrich (analytical grade) and** was **used without further**

treat- ment. 2.2. Adsorbent characterization The

15**CEC of** kaolin **was determined by the** proton exchange **method** and **the**

value is 67.9 meq/100 g. The surface structure crystallography of kaolin was measured on a Rigaku D/Max-2200 X-ray powder dif- fractometer with Cu/Ka (k = 0.154 nm) radiation. The diffraction intensities were recorded from 5 to 40°. Identification of functional groups of adsorbents

18**before and after adsorption were** conducted **using FTIR Spectrophotometer**

(Shimadzu 8400S). The chem- ical composition of kaolin and rarasaponin-kaolin was analyzed using Rigaku ZSX100e X-ray Fluorescence. 2.3. Extraction of rarasaponin Rarasaponin used in this study was obtained by extraction of dried fruits of S. rarak DC using water as solvent. The fruits were obtained from Klaten, Central Java, Indonesia. Dried fruits of S. rarak DC were crushed and sieved in the vibration screen (RETSCH) to obtain 180–200 mesh powder. Twenty grams of S. rarak DC powder was mixed with 200 mL of distilled water and then heated at 353 K for 60 min. The extract

42**was then centrifuged (Hettich Zentrifugen EBA-20)** for 10 min **at**

4000 rpm to separate solid from the solution. The supernatant was then concentrated by vacuum evaporation (BUCHI RE 121) and dried in a vacuum drying oven. The rarasaponin crystals were crushed and sieved using vibration screen (RETSCH) to obtain 180–200 mesh powder. 2.4. Modification of kaolin Modification of kaolin was conducted by soaking kaolin in rarasaponin solution for 24 h at 303 K under constant stirring at 500 rpm. After 24 h, the solution was centrifuged at 4500 rpm for 5 min to separate kaolin. Then rarasaponin-kaolin was dried in oven for 24 h, crushed and then was sieved using ASTM standard sieves to obtain 180–200 mesh particle size. 2.5. Adsorption isotherm experiment The adsorption isotherm experiments were con- ducted in static mode at 303, 318 and 333 K. A known amount of kaolin or rarasaponin-kaolin (0.1–1 g) was added to a series of 100 mL Erlenmeyer flasks contain- ing 50 mL of 800 ppm MG solution. The Erlenmeyer flask was then removed to shaking water bath and shaken at 200 rpm for 3 h at a desired temperature. After reaching equilibrium, the solution was centri- fuged at 4500 rpm for 5 min to separate the adsorbent from the solutions. The dye concentrations were deter- mined using UV-spectrophotometer at kmax = 616.4 nm, using a standard calibration graph. All

37**experiments were carried out in** triplicate. **The amount of** dye **adsorbed**

was calculated using formula qe ¼ ðC0 CeÞmV

20**where C0 and Ce are the** ini- tial **and equilibrium concentrations** (mg **/L)** of dye, respectively, **m** is **the** adsorbent **mass (g)** and **V is volume of the solution (L). 2.** 6. **Adsorption** kinetic experiment In adsorption kinetic study, 0.5 g of kaolin or rara- saponin-kaolin was added in 50 mL of 800 ppm MG solution at 303, 318 and 333 K. At certain time interval, MG concentrations were measured using UV-spectro- photometer at kmax = 616.4 nm, using a standard cali- bration graph.

46**All experiments were carried out in triplicate. 3. Results and discussion 3.1.** Adsorbent characterization **The** XRD spectra **for**

kaolin and rarasaponin-kaolin are depicted in Fig. 1. The basal spacing of kaolin and rarasaponin-kaolin was calculated based on Braggs diffraction equation k = 2d sin h, where k is wave- length, d is basal spacing (interlamelar spacing) and h is the angle, 2h is inversely proportional to d. The XRD spectra show that the angle of diffraction (2h) of Intensity 70 60 kaolin 50 rarasaponin-kaolin 40 30 20 10 0 10 11 12 13 14 15 2θ (o) Fig. 1. XRD spectra for kaolin and rarasaponin-kaolin. kaolin is 13.8272° and rarasaponin-kaolin is 11.3419°. occurred during modification process. After the These angles of diffraction correspond to basal adsorption process, the peaks at about 2,900 and spacing of 6.3992 for kaolin and 7.7952 for rarasapo- 1,400 cm 1 belong to carbonic structure of the dye nin-kaolin. The increase of basal spacing of rarasapo- which were observed in both adsorbents. The peak of nin-bentonite is possibly due to the intercalation of C–N stretch of MG structure was also observed at rarasaponin molecules into interlamelar spacing of wave number around 1100 cm 1. kaolin. The chemical composition of adsorbents was deter- mined using XRF analysis. Kaolin contains 15.1% 3.2. Adsorption isotherm study Al2O3; 67.5% SiO2; 1.13% K2O; 6.12% CaO; 0.47% Adsorption process is important for separation TiO2; 0.04% MnO; 8.86% Fe2O3; 0.1% BaO and 0.649% and purification of different kind of products in of other substances. After modification, the chemical process industry. Different kinds of adsorption mod- composition of rarasaponin-kaolin: 13.9% Al2O3; 66.2% els which were initially developed for gas phase SiO2; 1.37% K2O; 4.39% CaO; 0.43% TiO2; 0.04% MnO; adsorption in principle, can also be used for liquid 8.66% Fe2O3; 0.14% BaO and 4.931% of other sub- phase adsorption system. The most widely used iso- stances. The change of chemical composition of kaolin therms to correlate the adsorption equation in the is due to the presence of rarasaponin molecules in liquid phase are Langmuir and Freundlich. Other interlamelar spacing of kaolin. isotherms that are often used to correlate the liquid The surface functional groups of kaolin and rarasa- phase adsorption equilibria are Sip and Toth ponin-kaolin were characterized using FTIR analysis. equation. FTIR spectra for adsorbents before and after adsorp- Langmuir model was developed based on simple tion are depicted in Fig. 2. For easy reference, the assumptions [47]. The mathematical form of Langmuir wave numbers of each functional group present in model is as follow both adsorbent are also summarized in Table 1. Signif- icant difference of the peaks detected for rarasaponin- KLCe kaolin and kaolin before adsorption is in wave num- qLe ¼ qLmax ð1Þ bers 2,900, 1,400 and 1,700 cm 1, which are C–H 1 þ KLCe stretching, C–H bending and C=O stretching, respec- where qLmax is the maximum amount of adsorbate tively. These functional groups belong to carbon chain and carbonyl functional groups of rarasaponin. The adsorbed on the adsorbent surface (mmol/g); KL is the Langmuir constant (L/mmol); qLe is the amount of presence of these functional groups is strong indica- adsorbed dye per unit weight of adsorbent (mmol/g) tion that intercalation of rarasaponin molecules and Ce (mmol/L) is the equilibrium concentration. Fig. 2. FTIR spectra of kaolin after adsorption, kaolin before adsorption, rarasaponin-kaolin before adsorption and rarasaponin-kaolin after adsorption. Experimental adsorption equilibrium data are often collected at various temperatures; the tempera- ture dependent forms of Langmuir equation can be written as follow qLmax ¼ q0Lmax expðdðT0 TÞÞ KL ¼ KL0 exp E T0 T 1 RT0 ð2Þ ð3Þ here q0Lmax is the maximum Langmuir adsorption capacity at reference temperature (mmol/g), d is the temperature expansion coefficient of the adsorbate (K 1), KL0 is the Langmuir constant at reference tem- perature (L/mmol), E is the heat of adsorption (kJ) and T0 is the reference temperature (K) [48,49]. Freundlich model was developed based on assumption that adsorbent having heterogeneous sur- faces. The main drawback of this model is that it is only applicable at moderate range of concentration [48]. The Freundlich equation has the form qFre ¼ KFrC1e=n ð4Þ the temperature dependent forms of Freundlich model are KFr ¼ KFr0 exp aRT ð5Þ A0 1 n ¼ RT A0 ð6Þ where qFre

17**is the amount of adsorbed** dye **per unit weight of adsorbent (mmol/g);** KFr **is the Freundlich adsorption** capacity **(mmol/g)(L/mmol) n;** n **is the** heterogeneity **of the** system; A0 **is** a constant and KFr0 is the adsorption capacity at reference temperature T0. Table 1 The functional groups present in adsorbents Al(Mg)–OH stretching H–O–H

28**stretching C–** H **stretching C–** H **stretching C=O stretching** H **–O–** H bending **C–H bending C–** N **stretching Si–O–Si stretching Si–O stretching**

of silica quartz Al–Si–O bending Si–O–Si bending Raw kaolin 3,635 3,596 – – – 1,651 – – 1,085 783, 797 544 486 Rarasaponin- kaolin 3,623 3,539 2,929 2,859 1,721 1,643 1,461; 1,380 – 1,037 793 520 467, 476 Raw kaolin after adsorption 3,626 3,532 2,950 2,827 – 1,634 1,376 1,113 1,016 785 521 476 Rarasaponin-kaolin after adsorption 3,632 3,535 2,936 2,858 1,640 1,602 1,370 1,100 1,031 786 522 468 Sips isotherm is a combination of Freundlich and Langmuir equation [48,50]. Sips equation has the fol- lowing form qSe ¼ 1 þ ðKsCeÞ1 qSmaxðKsCeÞ1=n =n ð7Þ with its temperature dependent forms as follows: qSmax ¼ q0Smax expðdðT0 Ks ¼ Ks0 exp E T0 RT0 T n¼ 1 n10 þ gð1 TT0 Þ TÞÞ ð8Þ 1 ð9Þ ð10Þ where qSmax is the maximum amount of adsorbate adsorbed on the adsorbent surface (mmol/g); Ks is the Sips adsorption affinity constant (mmol/L)1/n; n is the heterogeneity of the system; qSe

40**is the amount of adsorbed** dye **per unit weight of adsorbent** (mmol **/g);** qS0max **is the maximum** Sips **adsorption capacity**

at refer- ence temperature (mmol/g); d is the temperature expansion coefficient of the adsorbate (K 1), Ks0 is the Sips constant at reference temperature (mmol/L)1/n; E

38**is the heat of adsorption (kJ);** T0 **is the**

reference temperature (K); g is a constant; and n0 is the hetero- geneity of the system at reference temperature. Another empirical equation also widely used to correlate the adsorption equilibria is Toth equation.

8**This equation describes well many systems with sub-monolayer coverage**

[48], and it has the following form: qTe ¼ ðKT þ CneÞ qTmaxCe 1=n ð11Þ like the other equations described previously, Toth equation also possesses the temperature dependent of equilibrium parameters as follows qTmax ¼ q0Tmax expðdðT0 TÞÞ KT ¼ KT0 exp E RT0 T0 T 1 n ¼ n0 þ gð1 T0 T Þ ð12Þ ð13Þ ð14Þ where qTmax is the maximum amount of adsorbate adsorbed on the adsorbent surface (mmol/g); KT is the Toth constant (mmol/L)n; n is the heterogeneity of the system; qTe

30**is the amount of adsorbed** dye **per unit weight of adsorbent** (mmol/g); **Ce** (mmol **/L) is** adsor- bate **equilibrium concentration;** q0Tmax **is the** maximum Toth **adsorption capacity**

at reference temperature (mmol/g), d is the temperature expansion coefficient of the adsorbate (K 1), KT0 is the Toth constant at ref- erence temperature (mmol/L)n, E

38**is the isosteric heat of adsorption (kJ);** T0 **is the**

reference temperature (K); g is a constant; and n0 is the heterogeneity of the sys- tem at reference temperature. The parameters of the models were

23**obtained by non-linear** least squares **fit of the** isotherm models **to the experimental** adsorption equilibria. **The**

calcula- tions were conducted for all temperatures of the adsorption equilibria simultaneously by using the fol- lowing Sum Square of Error (SSE) as the objective function to be minimized P !1=2 SSE ¼ ð ðqeðexpÞ qeðcalcÞÞ2Þ N ð15Þ where qe(exp) is the experimental amount of dye adsorbed, qe(calc) is the calculated amount of dye adsorbed using the isotherm model and N is the num- ber of experimental data. Figs. 3 and 4 show the adsorption experimental equilibria data of MG onto kaolin and rarasaponin- kaolin and those calculated using Langmuir, Freund- lich, Sips and Toth equations. The symbols represent the adsorption experimental data, while the solid lines represent the fitted models. The optimum parameters obtained from the above fitting procedure are summa- rized in Table 2. From Figs. 3 and 4, it can be seen that all the models can represent the adsorption experimental data well. However, to choose the cor- rect isotherm which can represent the experimental adsorption data, we cannot just depend on visual rep- resentation of the models or just based on the value of SSE, we should examine further the physical meaning of each parameters involved in the models. The cor- rect choice of the isotherm must be based on the con- sistency of physical meaning and reasonable value of the parameters. As mentioned before, the Langmuir equation was developed based on three simple assumptions and in large number of adsorption studies, this model can represent the data better than other isotherm equa- tions, also this model seems to represent the adsorp- tion equilibrium data of MG onto kaolin and rarasaponin-kaolin. Before we decide the applicability of this model to represent our adsorption experimen- tal data, we will discuss the physical meaning and consistency of the parameters. The parameter qL0max is 0,35 qe (mmol/g) 0,30 Langmuir Equation 0,25 0,20 0,15 0,10 303 K 0,05 318 K 333 K 0,00 0,35 0,0 0,2 0,4 0,6 0,8 1,0 1,2 1,4 1,6 Ce (mmol/L) 1,8 qe (mmol/g) 0,30 Sips Equation 0,25 0,20 0,15 0,10 0,05 0,00 303

3**K 318 K** 333 **K 0,0 0,2 0,4 0,6 0,8 1,0 1,2 1,4 1,6** Ce (mmol/L) **1,**

8 0,4 qe (mmol/g) 0,3 0,2 0,1 0,0 Freundlich Equation 303

3**K 318 K** 333 **K 0,** 35 **0,** 0 **0,** 2 **0,** 4 **0,** 6 0,8 **1,** 0 **1,** 2 **1,**

4 1,6 Ce (mmol/L) 1,8 qe (mmol/g) 0,30 Toth Equation 0,25 0,20 0,15 0,10 0,05 0,00 303

3**K 318 K** 333 **K 0,0 0,2 0,4 0,6 0,8 1,0 1,2 1,4**

Ce (mmol/L) 1,6 1,8 Fig. 3. Experimental adsorption equilibria data of MG onto kaolin and plots of adsorption models at various temperatures. 0,6 Langmuir Equation 0,5

16**qe (mmol/g) 0,4 0,3 0,2**

303

11**K 0,1** 318 **K** 333 **K 0,** 0 **0,** 0 **0,** 2 **0,** 4 **0,** 6 **0,**

8 1,0 1,2 1,4 1,6 Ce (mmol/L) 0,6 Sips Equation 0,5

16**qe (mmol/g) 0,4 0,3 0,2**

303

11**K 0,1** 318 **K** 333 **K 0,** 0 **0,** 0 **0,** 2 **0,** 4 **0,** 6 **0,**

8 1,0 1,2 1,4 1,6 Ce (mmol/L) 0,7 Freundlich Equation 0,6 0,5 qe (mmol/g) 0,4 0,3 0,2 303 K 318 K 0,1 333 K 0,0 0,0 0,2 0,4 0,6 0,8 1,0 1,2 1,4 1,6 Ce (mmol/L) 0,6 Toth Equation 0,5

16**qe (mmol/g) 0,4 0,3 0,2**

303

11**K 0,1** 318 **K** 333 **K 0,** 0 **0,** 0 **0,** 2 **0,** 4 **0,** 6 **0,**

8 1,0 1,2 1,4 1,6 Ce (mmol/L) Fig. 4. Experimental adsorption equilibria data of MG onto rarasaponin-kaolin and plots of adsorption models at various temperatures. the maximum Langmuir adsorption capacity at refer- ence temperature (25°C), and the values of this parameter for Kaolin and rarasaponin-kaolin are rea- sonable and consistent. The purpose of modification of Kaolin is to enhance its adsorption capability, and this phenomenon is caught by parameter q0Lmax , the value of this parameter for rarasaponin-kaolin is higher than in Kaolin, strong indication that the modi- fication of kaolin enhanced its adsorption capacity. Parameter d is the temperature expansion coeffi- cient of the adsorbate, the value of this parameter is specific for a given component and independent of the type of adsorbent [49]. From Table 2, it can be seen that the fitted value of parameter d by Langmuir model for kaolin and rarasaponin-kaolin is different. The values of parameter d for kaolin and rarasaponin- kaolin are 0.0038/K and 0.0062/K, respectively. The difference in values of parameter d for kaolin and rarasaponin-kaolin is an indication that the Langmuir parameter is not adequate for the system studied. In order to get better understanding, about the physical meaning of the Langmuir parameters, we will con- tinue our discussion for the remaining fitted parameters. Parameter E in Langmuir equation is the heat of adsorption, invariant with the surface loading [48].

7**When the heat of adsorption increases, the adsorbed amount increases due to the higher energy barrier that adsorbed molecules have to overcome to** diffuse **back to the**

bulk liquid. During modification of kaolin using rarasaponin, some of the rarasaponin molecules inter- calate to the interlayer spacing of kaolin and the inser- tion of the rarasaponin molecules increase the heterogeneity of the adsorbent. With the presence of another substance (rarasaponin) in the kaolin structure, other adsorption mechanisms also will occur, leading to the increase heat of adsorption. As depicted in Figs. 3 and 4, it is obvious that the adsorp- tion of MG onto Kaolin and rarasaponin-kaolin is con- trolled by physical adsorption mechanism. In physical adsorption mechanism, the uptake of adsorbate decreases with increase in temperature. Physical Table 2 Fitted parameters of adsorption equations Isotherm Langmuir Freundlich Sips Toth Parameters q0Lmax (mmol/g) d (K 1) E (kJ/mol) KL0 (L/mmol) SSE KF0 (mmol/g)(L/mmol) n a/A0 SSE q0Smax (mmol/g) d (K 1) KS0 (mmol/L)1/n E (kJ/mol) n0 g SSE q0Tmax (mmol/g) d (K 1) KT0 (mmol/L)n E (kJ/mol) n0 g SSE Kaolin 0.365 0.0038 21.83 4.392 0.006 8.974 0.0014 0.0024 0.509 0.0076 1.681 10.01 1.482 1.314 0.0016 0.709 0.0029 0.419 12.27 0.407 0.145 0.086 Rarasaponin-kaolin 0.497 0.0062 46.25 34.534 0.005 47.582 0.0018 0.0067 0.919 0.0079 2.410 21.72 2.370 1.405 0.0017 1.956 0.0271 0.253 8.76 0.151 2.321 0.042 adsorption processes usually have adsorption energies less than 40 kJ/mol, while higher energies (40–800 kJ/ mol) suggest chemisorptions. The fitted parameter E for kaolin is reasonable and consistent with the physi- cal meaning of this parameter, but not for rarasapo- nin-kaolin as seen in Table 2. The value of fitted parameter E for rarasaponin-kaolin suggests that the chemisorptions mechanism controls the process, a contradiction with the experimental data. Parameter KL0 is the Langmuir constant at refer- ence temperature. This parameter is also called as the affinity constant, which measures how strong adsor- bate molecules are attracted into surface of adsorbent [48]. When the affinity constant KL0 is larger, the inter- action of adsorbate molecules toward the adsorbent surface is stronger and the surface of adsorbent is cov- ered with more adsorbate molecules.

With the increase heterogeneity of the system, due to the inser- tion of rarasaponin molecules into interlayer structure of kaolin, the interaction of MG into rarasaponin-ben- tonite surface become stronger. This phenomenon was captured by the fitted parameter KL0 in Langmuir model, consistent and reasonable values of Langmuir affinity constant are observed as indicated in Table 2. The fitted affinity constant of Langmuir equation for rarasaponin-kaoilin is higher than kaolin. Even several parameters (q0Lmax and KL0) are reasonable and have consistent physical meaning, the failure of parameters E and d to give consistent physical meaning are indi- cation that the Langmuir model is not adequate to correlate the adsorption experimental data of MG onto kaolin and rarasaponin-kaolin. Similar to the Langmuir model, the fitted parame- ters KFr0 (Freundlich), (Sips model) and q0Tmax (Toth equation) represent the maximum adsorption capac- ity. Consistent and reasonable parameter values of maximum adsorption capacity were obtained for both Sips and Toth models, but not for Freundlich model as given in Table 2. Since the Freundlich equation fails to give reasonable value for the adsorption capacity parameter, it will not be included in further discussion. As expected, the fitted parameter q0Smax (Sips model) and q0Tmax (Toth equation) for rarasaponin-kaolin are higher than kaolin. As mentioned before, the parameter d is the temperature expansion coefficient of the adsorbate and its value must be positive and specific for a given component and does not depend on the type of adsorbent. The fitted parameter d of Sips model for both kaolin and rarasaponin kaolin is essentially constant and of the order of 10 3 K 1, consistent with the value of many adsorbate [49]. Toth equation failed to give consistent and reasonable result of this fitted parameter as seen in Table 2. The purpose of kaolin modification is to enhance its adsorption capacity. The adsorption capacity of rarasaponin-kaolin towards MG is higher than origi- nal kaolin. When the amount of MG uptake increases, the

7**surface is covered more with** MG molecules **as a result of the stronger affinity of** MG **molecule towards the surface** of rarasaponin-kaolin. **The** fitted parameter **of adsorption**

affinity of Sips model obeys this phe- nomenon and the opposite behaviour was observed for Toth model as indicated in Table 2. As mentioned in previous paragraph, the increase in the amount of MG uptake causes the increase of heat of adsorption

8**due to the higher energy barrier that adsorbed** mole- cules **have to overcome to** diffuse **back to the**

bulk liquid [48], therefore, the adsorption energy of MG onto rarasaponin-kaolin should be higher than the adsorption energy of MG onto kaolin. This phenome- non was caught by fitted parameter E of Sips model, while the Toth equation failed to give consistent value of this parameter. These evidences clearly indicate that Toth model is not suitable for correlating the adsorption experimental data of MG onto kaolin or rarasaponin-kaolin. The parameter n0 in Sips model

8**could be regarded as the parameter characterizing the system** heterogene- ity. If **the**

value of n0 is more deviate

42**from unity, the system is more heterogeneous. The**

intercalation of rarasaponin molecules into kaolin structure increases the heterogeneity of the system and the fitted parame- ter n0 of Sips model

26**is consistent with the physical meaning of this parameter.**

Based on the evaluation, of the physical meaning of fitted parameters of each equa- tion, it is clear that the Sips equation can represent the adsorption data better than the other equations. 3.3. Adsorption kinetic study To properly design an adsorption system, addi- tional information besides adsorption equilibria is needed and that necessary information is the adsorp- tion kinetics [48,51]. Numerous kinetic models are available for the prediction of behaviour of kinetic experimental data. Most widely used models are

24**pseudo-first-order** [52] **and pseudo-second-order** [53]. **Pseudo-first-order model is the**

earliest known model, describing the rate of sorption in the liquid phase system [51], and this model has the following form: dqt dt ¼ k1ðqe qtÞ ð16Þ where k1 is

21**rate constant of pseudo-** first **-order reaction (min** 1); qe **is the amount of** adsorbate adsorbed **at equilibrium** (mmol **/g) and** qt **is the amount of** adsor- bate adsorbed **at** certain **time** (mmol **/g).**

Integration of Eq. (16) yield: qt ¼ qeð1 expð k1tÞÞ ð17Þ

34**Pseudo-second-order model was developed by Blanchard et al.**

[53], to describe the kinetics of heavy metal removal by natural zeolites. This model is usu- ally associated with the situation when the rate of direct adsorption/desorption process controls the overall sorption kinetics [51].

34**The mathematical form of the pseudo-second-order**

is d dtt ¼ k2ðqe q qt Þ2 ð18Þ where k2 is rate constant of pseudo-second-order model (g/mmol min 1). Integration of Eq. (18) yield: qek2t qt ¼ qe 1 þ qek2t ð19Þ The adsorption kinetic experimental data

25**and the fitted** model **of pseudo-first and pseudo-second-order**

of MG onto kaolin and rarasaponin-kaolin are given in Figs. 5 and 6, respectively. The fitted parameters of

10**pseudo-first and** pseudo **-second-order models are summarized in Table 3** for kaolin **and Table**

4 for rara- saponin-kaolin. Visually, both of these models

26**can represent the experimental data well as** indicated **in** Figs. **5** and 6. However, **the** calculated values **of** qe values **from**

pseudo-second-order deviate quite large from experimental data. Pseudo-first-order gives rea- sonable values of the fitted parameters as indicated in Tables 3 and 4. Better fitted values obtained for pseudo-first-order than pseudo-second-order also an indication that physical adsorption mechanism was more dominant than chemisorptions. As mentioned by Plazinski et al. [51], the pseudo-second-order is associated with the situation when the rate of direct adsorption/desorption process is seen as a kind of chemical reaction; while the pseudo-first-order was developed based on the assumption that overall rate of sorption was determined by the rate of direct solute transfer from the solution to the adsorbed phase (a) 0,20 (a) 0,25 0,18 0,16 0,20 0,14 qt (mmol/g) 0,12 0,15 0,10 0,08 qt (mmol/g) 0,10 0,06 303 K 0,04 318 K 0,05 303 K 333 K 318 K 0,02 333 K 0,00 0,00 0 50 100 150 200 250 0 50 100 150 200 250 Time (minutes) Time (minutes) (b) 0,20 0,25 (b) 0,15 qt (mmol/g) 0

33**,10 0,05** 303 **K** 318 **K** 333 **K 0,00 0**

50 100 150 200 250 Time (minutes) Fig. 5. The adsorption kinetic experimental data of MG onto kaolin and model fitted of

31**(a) pseudo-first-order and (b) pseudo-second-order.**

(physical interaction between adsorbate and adsorbent). 3.4. Adsorption thermodynamic To get a complete feature of the adsorption MG onto kaolin and rarasaponin-kaolin, thermodynamic study was also conducted.

13**Thermodynamic properties like standard Gibb’s free energy change**

(DG0), stan- Table 3 The adsorption kinetic parameters of MG onto kaolin 0,20 qt (mmol/g) 0,15 0

33**,10 0,05** 303 **K** 318 **K** 333 **K 0,00 0**

50 100 150 200 250 Time (minutes) Fig. 6. The adsorption kinetic experimental data of MG onto rarasaponin-kaolin and model fitted of

31**(a) pseudo- first-order and (b) pseudo-second-order.**

dard enthalpy change (DH0) and standard entropy change (DS0) of the adsorption of MG onto kaolin and rarasaponin-kaolin were investigated. The standard Gibbs free energy (DG0) at a constant temperature can be calculated using the following formula G0 ¼ RTlnKd ð20Þ where Kd is thermodynamic distribution coefficient. The values of Kd were obtained by plotting qe as x- Temperature qexp (mmol/g) 30°C 0.1796 45°C 0.1677 60°C 0.1576 Pseudo-first

45**-order qe (mmol/g) k1 (min 1) r2 0.** 1810 **0.** 0231 **0.** 9987 **0.** 2156 **0.** 1260 **0.** 9964 **0.** 1734 **0.**

0201 0.9975 0.2134 0.0991 0.9913 0.1607 0.0188 0.9974 0.2065 0.0845 0.9941 Pseudo-second-order

12**qe (mmol/g) k2 (g mmol 1 min 1) r2**

Table 4 The

37**adsorption kinetic parameters of MG onto** rarasaponin-kaolin **Temperature** 30 **°C**

45°C 60°C qexp (mmol/g) 0.2158 0.2122 0.1994

29**Pseudo-first-order qe** (mmol **/g) k1 (min 1) r2** 0.2155 **0.** 0313 **0.** 9964 **0.** 2106 **0.** 0276 **0.** 9985 **0.** 2012 **0.** 0225 **0.** 9981 **Pseudo-second-order** qe (mmol **/g)**

12**k2 (g mmol min 1) r2** 0.2507 **0.** 1541 **0.** 9916 **0.** 2524 **0.** 1210 **0.** 9968 0.2454 **0.**

1001 0.9939 Table 5 Thermodynamic parameters of MG adsorption onto kaolin and rarasaponin-kaolin T (K) Kaolin

14**DH0 (kJ/mol) DS0** (kJ **/mol./K)** Di0 **(kJ/mol)**

303 318 333 29.81 0.09 2.25 0.88 0.48 Rarasaponin-kaolin

14**DH0 (kJ/mol) DS0** (kJ **/mol.K) DG0 (kJ/mol)**

61.62 0.17 9.12 6.52 3.92 axis, ln (qe/Ce) as y-axis and the intercept is the value of ln Kd. Based on van’t Hoff equation, standard enthalpy change (DH0) and standard entropy change (DS0) are correlated to the thermodynamic distribution coefficient (Kd) H0 S0 RT R ¼ ln Kd ð21Þ by plotting 1/T vs. ln Kd, the

14**values of DH0 and DS0** can be obtained. **The**

thermodynamic parameters obtained

14**from Eqs.** (20) **and** (21) **are** summarized **in Table** 5. DH0 **values**

for both kaolin and rarasaponin- kaolin are negative indicating that the adsorption of MG onto both adsorbents is exothermic and the increase in temperature will decrease the uptake of the adsorbate. The DS0 for kaolin and rarasaponin- kaolin are both negative due to interaction between adsorbate and adsorbent that made the system less disorder. DG0 is the most important parameter to determine whether the adsorption occurs spontane- ously.

35**The negative value of** DG0 indicates **that the adsorption of MG**

onto kaolin and rarasaponin-kaolin occurrs spontaneously. The increase of DG0 value

8**with temperature indicates that the adsorption** of MG **is** less favourable **at**

high temperature. 4. Conclusion Modification of Kaolin using natural surfactant rarasaponin increases the adsorption capability of kao- lin. The adsorption experimental data were correlated using Langmuir, Freundlich, Sips and Toth equations. Sips model gave consistent and reasonable values of the fitted parameters. The

13**pseudo-first-order gave** bet- ter **correlation for** the adsorption **kinetic**

of MG onto kaolin and rarasaponin-kaolin. Thermodynamic prop- erties

13**like standard Gibb’s free energy change** (DG0), **standard enthalpy change** (DH0) **and standard entropy change** (DS0) **of the**

adsorption of MG onto kaolin and rarasaponin-kaolin were obtained in this study. References [1] P. Nigam, G. Armour, I.M. Banat, D. Singh, D. Singh, R. Marchant, Physical removal of textile dyes and solid state fermentation of dye adsorbed agricultural residues, Bioresour. Technol. 72 (2000) 219–226. [2] S.J. Allen, Q. Gan, R. Matthews, P.A. Johnson, Kinetic model- ing of the adsorption of basic dyes by kudzu, J. Colloid Interf. Sci. 286 (2005) 101–109. [3] G. Crini, H.N. Peindy, F. Gimbert, C. Robert, Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solution by adsorption using cyclodextrin based adsorbent: Kinetic and equilibrium studies, Sep. Purif. Technol. 53 (2007) 97–110. [4] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various car- bons—a comparative study, Dyes Pigments 51 (2001) 25–40. [5] V. Vimonsesa, S. Lei, B. Jin, C.W.K. Chow, C. 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