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25Renewable rarasaponin-bentonite-alginate composite with sponge-like structure and its application for crystal violet removal from aqueous solution

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2737 6644, email: jindranyoo@yahoo.com (J.N. Putro), alfin_kur@yahoo.com (A. Kurniawan) Received 6 October 2018; Accepted 31 March 2019 abstract Adsorption is an efficient process for removing contaminants from water by using adsorbent. In this work, bentonite, rarasaponin, and sodium alginate are used as raw materials to prepare new composite to be applied

16to the adsorption of crystal violet dye. The

prepared adsorbent (bentonite-rarasaponin-alginate composite) has a sponge-like appearance. The Fourier transform infrared (FTIR), X-ray diffraction (XRD), nitrogen (N₂) sorption and scanning electron microscopy (SEM) methods were employed to characterize the prepared adsorbents. The

29adsorption experiments were conducted isothermally at 30,50, and 70°C

. The

5 Freundlich and Langmuir isotherm models were chosen to correlate the equilibrium adsorption data. Meanwhile, **the**

adsorption kinetics was studied

5 at 30°C, and the **data were** correlated by **using the pseudo-first-order and pseudo-second-order**. Based on **the adsorption** results, it **was found**

that composite can adsorb crystal violet dye 3 times more than bentonite at all investigated temperatures, where at 70°C the adsorption capacity for acid-activated bentonite is 176.63 mg/g and for rarasaponin-bentonite-alginate composite is 476.04 mg/g. The

22 adsorption of crystal violet dye onto the adsorbents increases with increasing

temperature indicating that the chemisorption is dominant in this process. Keywords: Acid activated bentonite; Rarasaponin; Sodium alginate; Composite; Isotherms; Kinetics 1. Introduction Contamination of surface water by synthetic dyes is a serious environmental problem. Most of these contaminants come from the effluent of textile industries. Some of the synthetic dyes are found to be

6 resistant to microbial degradation, causing **their presence in water** environment **harmful to**

aquatic organisms. Some techniques can be employed to remove the synthetic dyes from water, some of them are biological treatment, coagulation, floatation, oxidation, ozonation, nanofiltration, and adsorption [1–3]. Among the techniques available, adsorption is used more often because this technique is inexpensive, environmentally friendly, and more importantly effective against most types of contaminants [4]. The success of the adsorption process which is indicated by the high removal of contaminant is strongly influenced by the type adsorbent. Activated carbon is a commercial adsorbent with good surface reactivity which is often used especially for the separation and purification of water from organic compounds such as syn- 1944-3994 /

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. L. Laysandra et al. / Desalination and Water Treatment 160 (2019) 354–365 synthetic dyes. However, the commercially available activated carbons are expensive; therefore the use of activated carbon for water and wastewater treatment is economically unfeasible. To overcome this, the developments of alternatively low-cost adsorbents which are inexpensive, harmless, and have high adsorption capacity are needed [5–7]. Bentonite mainly consists of smectite montmorillonite, bentonite also commonly called as montmorillonite. The natural and chemically modified bentonites are well known as alternative cheap adsorbents, they have large

5 Brunauer-Emmett-Teller (BET) surface area

due to its layered structure. The adsorption affinity of bentonite can be increased by modifying it with an intercalating agent (i.e., surfactant). The affinity enhancement enables bentonite to be employed for a wider variety of pollutants [8]. In order to avoid environmental problems that might arise from the use of synthetic surfactants, the use of an environmentally friendly (natural) surfactant is more desirable [9]. Some studies related to adsorption properties of intercalated bentonite have been reported. A study by Kurniawan et al. reported that bentonite intercalated with the extract from *Sapindus rarak* DC (rarasaponin) can adsorb 256 mg Methylene Blue per g adsorbent (at 60°C), while raw bentonite can only adsorb 194 mg methylene blue per g adsorbent (at 60°C) [9]. Fosso-Kankeu et al. reported that bentonite intercalated by cationic surfactant hexadecyltrimethyl ammonium bromide can adsorb 16.04 mg Congo Red per g of adsorbent, while the natural bentonite can adsorb 5.00 mg Congo Red per g of adsorbent [10]; Özcan et al. reported that bentonite intercalated with cationic surfactant dodecyltrimethyl ammonium bromide can adsorb 206.58 mg Reactive Blue 19 per g adsorbent [11]. Study on the intercalation of cetyltrimethyl ammonium bromide (CTAB) into another type of clay mineral, namely kaolin, by Zenasni et al., also showed that CTAB-kaolin can adsorb 24.46 mg Congo Red per g adsorbent which is 4 times higher than natural kaolin (5.94 mg Congo Red per g adsorbent) [12]. In this work, rarasaponin is used as a surfactant for intercalation. Intercalation process can increase the number of active sites, surface area and interlayer spacing of natural bentonite. The intercalation of rarasaponin molecules into the interlayer of bentonite occurs in several stages; the first stage is deacylation of rarasaponin due to the dissolution in the polar solvent, this causes rarasaponin to be negatively charged; the second stage is protonation of the silanol group on bentonite so that the bentonite is positively charged; and the last stage is charge balancing through the interaction between the two differently charged molecules [13]. In this work, a natural polymer, sodium alginate, is combined with rarasaponin-bentonite

5in order to further increase **the adsorption** capacity. **The main purpose of**

this work is to prepare a new, low-cost, and environmentally friendly adsorbent composite with high adsorption capacity for the removal of organic dye from aqueous solution. Some analyses including

1FTIR, XRD, SEM, **and nitrogen sorption were employed** prior to characterizing **the**

prepared rarasaponin-bentonite-alginate composites. The formation mechanism of the composite is also given in this manuscript. The adsorption ability of the composites was investigated against a cationic dye, Crystal Violet. The adsorption was conducted isothermally and kinetically.

202. Materials and methods 2.1. Materials **The bentonite used in this study is**

natural calcium-exchanged bentonite (Ca-bentonite)

2obtained from the **mining site at Pacitan, East Java, Indonesia**

. *Sapindus rarak* DC was

2obtained from **Klaten, Central Java, Indonesia. The natural surfactant, rarasaponin**

, was obtained by extracting the fruit pericarp of Sapindus rarak DC. The detailed procedure of rarasaponin extraction can be seen elsewhere [9]. Sodium alginate was supplied from CV. Nura Jaya, Surabaya, Indonesia. Analytical grade crystal violet (purity > 90%, C₂₅H₃₀Cl, Mw 407.98 g/mol) was purchased from Sigma Aldrich, Singapore. The chemicals are used as received without further purification. 2.2. Preparation of rarasaponin-bentonite and rarasaponin-bentonite-alginate composite Ca-bentonite was acid-activated by mixing with 5 N H₂SO₄ solution (1:10 w/v ratio) under constant stirring at 500 rpm and 70°C for 2 h. The acid-activated bentonite

14 was rinsed with **distilled water until the pH of the** rinse water **was**

constant. Subsequently, the acid-activated bentonite was dried at 105°C

17 in an oven (Mettler UM 400) for 24 h. The dried acid-activated **bentonite was** pulverized **into powder**

and

3 sieved using vibration screener (Retsch AS 200) to obtain a particle size of -180/+200 **mesh**. The rarasaponin-**bentonite**

was synthesized

7 according to the procedure reported by Kurniawan et al

. (2012) [14], briefly

2 g of rarasaponin was dissolved into 50 mL **distilled water**, then **10 g of acid-** activated **bentonite was added to the solution**. Rarasaponin **was**

dissolved in advance with the aim of increasing the contact surface area between rarasaponin and acid-activated bentonite. After mixing, the mixture was irradiated

17 in a microwave oven at 700 W (National NN-S327 WF) for 3 min. The rarasaponin-**bentonite**

-alginate composite was prepared according to the same procedure [14] as rarasaponin-bentonite with slight modification; briefly 0.45 g of rarasaponin was mixed with 25 mL distilled water. The rarasaponin solution was vigorously stirred until the rarasaponin solution is foamy. Subsequently, acid-activated bentonite was added to the rarasaponin solution with a mass ratio of acid-activated bentonite to rarasaponin of 10:1. The mixture was stirred at 500 rpm for 10 min, and then 0.

25 g of sodium alginate was added to the mixture. **The mixture**

of sodium alginate, acid activated bentonite, and rarasaponin was then

1 heated at 70°C under constant stirring at 800 rpm for 1 h. After the

heating, mixture slurry was obtained and then slowly transferred into 200 mL of 0.3 N CaCl₂ solution to form granules rarasaponin-bentonite-alginate composite. The excess CaCl₂ on the surface of the composite was repeatedly washed using reverse osmosis

7 water and dried in an oven at 50°C for 12 h. 2.3. Characterization of the
The characterization **of the**

samples, namely acid-activated bentonite, rarasaponin-bentonite, and rarasaponin-bentonite-alginate composite, was conducted by using L. Laysandra et al. / Desalination and Water Treatment 160 (2019) 354–365 Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), SEM (scanning electron microscopy), and nitrogen sorption methods. The FTIR analysis was carried out using FTIR SHI-MADZU 8400S, KBr pellet method was employed to obtain the spectra of the samples. The spectra were scanned at a wavelength range of 4000–400 cm⁻¹ with a resolution of 2 cm⁻¹. The

21 XRD analysis was conducted by using a Philips X'pert X-ray Diffractometer. The XRD patterns were acquired at 40 kV and 30 mA

with

3 Cu Kα1 (λ = 0.15405 nm) as the source of radiation. The

surface topography was obtained by using

3a JEOL JSM-6500 F field emission SEM at 10 kV

and WD 10.1 to 10.3 mm. Prior for SEM, the

1 samples were coated with thin layer (3 nm) of platinum

/palladium (Pt/Pd) alloy using an auto fine coater JEC-3000 F. The coating process was carried out in Argon atmosphere for 90 s. The BET surface area was determined by using automatic sorption analyzer Micromeritics ASAP 2010. The measurements were conducted at -195.8°C (boiling point of nitrogen) over a relative pressure of 0.001–0.995. The samples were degassed at 150°C under high vacuum before each measurement. The BET surface area was calculated at a relative pressure in the range of 0.05–0.35. The point of zero charge (pH_{pzc}) of each adsorbent used in this study

4 was determined by using the pH drift method

[15], and it was found that pH_{pzc} of acid-activated bentonite is 3.08, rarasaponin-bentonite is 3.44, and the rarasaponin-bentonite-alginate composite is 4.08. 2.4. Adsorption of dye The optimal pH for the adsorption of crystal violet onto the prepared adsorbents is studied in the pH range of 2–10, with initial crystal violet concentration of 800 ppm, a temperature of $30 \pm 1^\circ\text{C}$, for 8 h. The

26 **pH was adjusted using 0.1 N of HCl or NaOH solutions. After equilibrium, the adsorbent was separated by** using a centrifuge, **and the**

concentration of un-adsorbed crystal violet in the filtrate was then

10 **analyzed using Shimadzu UV/Vis-1700 spectrophotometer at a wavelength of 590 nm. The**

adsorption equilibrium experiments were performed in batch. A stock solution of 800 ppm crystal violet dye at a certain pH was prepared by dissolving a certain amount of crystal violet in 1000 mL distilled water. Subsequently, the crystal violet

23 **solution was distributed in a series of Erlenmeyer flasks (50 mL of solution in each flask). A**

various mass of adsorbent was then introduced to the series of Erlenmeyer flasks.

4 **The adsorption was conducted for 8 h in a Memmert shaking water bath**

at various temperatures of $30, 50, 70 \pm 1^\circ\text{C}$. After adsorption, the solution was centrifuged at 4700

31 **rpm for 5 min to separate the solution from solid adsorbent particles. The concentration of crystal violet in the solution**

before and after the adsorption process was measured

7 **using a Shimadzu UV/Vis-1700 spectrophotometer at maximum absorbance wavelengths of 590 nm**

28 **All adsorption experiments were repeated at least three times to ensure the accuracy of the obtained data. The**

dye removal efficiency was calculated in percentage by using Eq. (1), while the amount of crystal violet

30adsorbed at equilibrium condition was calculated by using Eq. (2)

). % dye removal = $(C_i - C_e) \times 100$ $q_e = (C_i - C_e) \times$

2V m (2) where q_e is the amount of dye adsorbed at equilibrium (mg/g adsorbent), C_i and C_e (mg/L) are the

initial and equilibrium crystal violet dye concentration,

15respectively, V (L) is the volume of the dye solution, and m (g) is the mass of the adsorbent. For the kinetic adsorption experiments, 0.5 g of the adsorbent was introduced into a series of 50 mL crystal violet solution with various initial concentrations

(600, 800, and 1000 ppm). The adsorption was performed in a shaker water bath (

14200 rpm), and a temperature of 30°C. The kinetic adsorption data were

collected by taking one of the samples at a certain period of time. The

29solid adsorbent was then separated from the filtrate by using centrifugation technique. The concentration of

remaining crystal violet dye in the filtrate was measured quantitatively by using a spectrophotometer. The amount of crystal violet adsorbed onto adsorbent at a certain time (t) was calculated using Eq. (3). $q_t = (C_i - C_t) \times V$ (3) where C_t is the crystal violet concentration in the solution at time t. 2.5. Goodness of fitting analysis The goodness of fitting between experimental data and calculated data for each non-linear adsorption models is measured by determining the coefficient of determination (R^2), hybrid fractional error function (HYBRID), and Marquardt's percent standard deviation (MPSD) [16,17]. The R^2 shows the measurement of how close the fitting of experimental data is to the calculated data, this coefficient has a degree in the range of 0–1. The HYBRID error function is an improvement to that of classic error function namely sum of squared errors (SSE), the improvement is especially at to minimize the magnitude of the errors at a lower level of liquid-phase concentration. The MPSD is an error function that shows the geometric mean error based on the number of degree of freedom in the investigated system [16–19]. 3. Result and discussion For the purpose of simplification, acid-activated bentonite, rarasaponin-bentonite, and rarasaponin-bentonite-alginate are abbreviated as AAB, RB, and RBA, respectively. 3.1. Characterization of the adsorbents The FTIR spectra of AAB, RB, and RBA composite are shown in Fig. 1. Both RB and RBA composite possesses spectra originated from rarasaponin and bentonite. There are some slight shifts observed for the spectra of RBA composite compared with RB. The broad band corresponds to

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8et al. / Desalination and Water Treatment 160 (2019) 354–365 Fig. 1. FTIR spectra of (a) AAB, (b) RB, and

(c) RBA composite. the stretching of the –OH (hydroxyl) groups are found at the wavenumber of 3629.78, 3627.85 and 3625.92 cm^{-1} for AAB, RB, and RBA composite, respectively. Bands at 3278.76 (AAB), 3274.90 (RB), and 3272.98 (RBA composite) cm^{-1} responsible for the vibration of –OH stretching which represents the bond between –OH group and Al or Si. The presence of rarasaponin is indicated by the appearance of the band at 1710.74 and 1708.81 cm^{-1} for RB and RBA composite, respectively, where the bands are attributed to the stretching vibration of C=O bonds; these bands also indicate ions exchange between Ca^{+2} from bentonite against the acetyl cation ($\text{C}_2\text{H}_3\text{O}^+$) from rarasaponin [9]. The –OH bending of H_2O at interlayer of bentonite is indicated by the peaks at 1654.81 cm^{-1} for AAB, 1627.81 cm^{-1} for RB and 1639.38 cm^{-1} for RBA composite. The Al–Al–OH bending vibration was observed at 916.12 (AAB), 914.20 (RB), and 916.12 cm^{-1} (RBA composite); Al–O–Si bending vibration was observed at 702.04 (AAB), 696.25 (RB), and 698.18 cm^{-1} (RBA composite); and Si–O–Si bending vibration was observed at 470.60 (AAB), 447.45 (RB), and 476.38 cm^{-1} (RBA composite). Alginate compound was added for the preparation of the RBA composite. The interaction of alginate with rarasaponin/bentonite was indicated from the appearance of new bands at 1529.45 and 1454.23 cm^{-1} , where these bands correspond to the asymmetrical and symmetrical stretching vibrations of the carboxylic groups ($-\text{COO}-$). The bands also indicate that the alginate molecules have successfully binded to the silanol group by releasing cationic Na^+ from sodium alginate compound. For easy reference, the wave-number values and their corresponding surface functional groups are tabulated in Table 1. The X-ray diffraction (

13XRD) spectra of the solid adsorbents are given in Fig. 2. The

intercalation of rarasaponin to the interlayer of bentonite leads to the shift of basal spacing of bentonite. Originally, the AAB has a d spacing (001) of 1.36 nm. The intercalation of rarasaponin causes the d spacing to increase to 1.54 nm and 1.58 nm for RB and RBA composite, respectively. Some characteristic peaks of quartz are also observed in Fig. 2. The surface topographies of the adsorbents were observed by using SEM and the images are depicted in Fig. 3. Different surface morphologies are observed for AAB, RB, and RBA composite. Table 1 Surface functional groups of the AAB, RB, and RBA composite

Functional group	Wave number (cm^{-1})
AAB	3629.78
RB	3627.85
RBA composite	3625.92
-OH stretching in the hydroxyl group	3629.78 3627.85 3625.92
-OH stretch of (Al or Si)	3278.76 3274.90 3272.98
-OH group	1710.74 1708.81
-OH bending of H_2O at interlayer	1654.81 1627.81 1639.38
bentonite for adsorbed Al-Al-OH bend	916.12 914.20 916.12
Al-O-Si bend	702.04 696.25 698.18
Si-O-Si bend	470.60 447.45 476.38
C=O stretch ($\text{C}_2\text{H}_3\text{O}^+$)	1529.45 1454.23
COO- asymmetrical stretching	1529.45
COO- symmetric stretching	1454.23

alginate Fig. 2. X-ray diffraction spectra of (a) AAB, (b) RB, and (c) RBA composite. RB, and RBA composite. The SEM images of RB (Fig. 3b) and RBA composite (Fig. 3c) show a larger particle size compared to AAB (Fig. 3a); this indicates that the addition of alginate, as well as rarasaponin, causes the bentonite particles to join and form larger particles. The addition of rarasaponin (in the formation of RB) only produced a weak interaction between the rarasaponin and bentonite thus the RB still have a powder form (bigger than AAB). In the formation of RBA composite, the addition of alginate causes the RB particles to join together with a stronger interaction to form larger particles which have a sponge-like structure (Fig. 3d). L. Laysandra et al. / Desalination and Water Treatment 160 (2019) 354–365

19Fig. 3. SEM topography images of (a) AAB, (b) RB, and (c)

) RBA composite. Image (d) show the digital photograph of the RBA composite. The

4nitrogen sorption isotherms of the AAB, RB, and RBA composite are given in Fig

4. All of the adsorbents performed a

3 rapid intake of nitrogen gas molecules at a low relative pressure (p

$/p_0$). This phenomenon indicates that all of the adsorbents have a microporous structure (type I isotherm). Broad hysteresis loops at p/p_0 above 0.4 suggest that the adsorbents also have a mesoporous structure (type II isotherm). RB and RBA possess broader hysteresis loop than AAB, where RB has the broadest loop. The broad hysteresis loop indicates that the intercalation of rarasaponin into interlayer of bentonite created the more complex structure with some interconnected interlayer. The BET surface area for AAB, RB, and RBA composite is 73.7 m²/g, 88.

73 m²/g, and **97.8 m²/g**, respectively. The **pore volume**

of AAB, RB, and RBA composite is 0.121 cm³/g, 0.376 cm³/g, and 0.392 cm³/g, respectively. 3.2.

22 Effect of pH on the adsorption of crystal violet onto the adsorbents The **adsorption of crystal violet on the**

surface of the adsorbents is very

6 dependent on the pH of the solution. The pH of the solution affects the surface charge of the adsorbents and also the regulation of ionization of the adsorbate. The

point

10 zero charge (pH_{pzc}) of the adsorbents are depicted in Fig. **5**

, where AAB, RB, and RBA composite have pH_{pzc} of 3.20, 3.40, and 4.06, respectively. The adsorbent will have a positive surface charge when the pH of the solution below Fig. 4. Nitrogen sorption isotherms of AAB, RB, and RBA composite. their pH_{pzc}, and have

23 a negative surface charge at the pH above the

pH_{pzc}. The

1 effect of pH on the adsorption of crystal violet onto AAB, RB, and

RBA composite

20 can be seen in Fig. 6. The adsorption capacity of

the adsorbents increases at the pHs above their pH_{pzc}. At pH below pH_{pzc}, the interaction between cationic crystal violet dye and positively charged L. Laysandra et al. / Desalination and Water Treatment 160 (2019) 354–365 Fig. 5. The point of zero charges (pH_{pzc}) of (a) AAB, (b) RB, and (c) RBA composite. Fig. 6. Effect of pH on the adsorption of crystal violet onto AAB, RB, and RBA composite. bentonite leading to repulsion of the dye from the surface of the adsorbents thus decrease the adsorption capacity. At pH above pH_{pzc}, the electrostatic attraction force between cationic crystal violet and negatively charged bentonite occurred thus leading to the higher amount of the dye attached onto the surface of the adsorbents. As the pH increases, the silanol group of bentonite became deprotonated thus increasing the number of negative sites on the surface of adsorbents [20]. The highest removal efficiency of crystal violet was found to be 90% for AAB, 96.32 % for RB, and 99.89% for RBA composite. 3.3. The formation mechanism of RBA composite The formation mechanism of RB by intercalating bentonite with rarasaponin has been described by Kurniawan et al. 2011 [9]. The formation mechanism of the RBA composite by combining RB and sodium alginate is presented in this section. The schematic of the proposed formation mechanism is presented in Fig. 7. The formation mechanism of RBA composite occurred as follow: in the AAB molecules, the silanol group on the tetrahedral layer of AAB is

2protonated by the occurrence of H⁺ion since the pH_{solution} < pH_{pzc}, therefore the –OH of

silanol group is protonated into –H₂O⁺. In the rarasaponin molecules, dissolution of rarasaponin in the water cause the two acyl groups (at carbonyl structure) to be deacylated and produced sites with a negative charge. These negatively charged sites are the active binding sites against the positively charged bentonite. As for the natural polymer sodium alginate (Na-alginate), the Na⁺ ion attached to the carboxyl structure will be released L. Laysandra et al. / Desalination and Water Treatment 160 (2019) 354–365 Fig. 7. The proposed formation mechanism of rarasaponin-bentonite-alginate (RBA) composite. as it is dissolved in water and produced an anionic polymer with the negatively charged carboxyl group(–COO[–]) [21]. The –COO[–] group also contributes as an active binding site for positively charged bentonite. The addition of alginate also induced a gelation process; thus the rarasaponin/ bentonite particles are attracted together. The final step, the rarasaponin/bentonite/alginate mixture is transferred into CaCl₂ solution. The Ca²⁺ ions from CaCl₂ are induced cross-linking between the alginate polymers and produced a rigid gel, where the cross linking occurs between the unbinding –COO[–] groups of the alginate with the pattern of –COO[–]Ca²⁺–COO[–] [22]. 3.4. Equilibrium

12adsorption isotherm studies The equilibrium adsorption isotherm model scan describe how the adsorbate molecules distributed in the

solution. The models also can be used to determine the parameters L. Laysandra

8et al. / Desalination and Water Treatment 160 (2019)

) 354–365 in adsorption equilibrium [23,24]. Langmuir and Freundlich adsorption models were employed to investigate the adsorption equilibria data in a single system at three different temperature of 30, 50, and 70°C. The Langmuir model describes the mono layer adsorption on the homogeneous surface. The Langmuir equation is written as follows: $q_e = q_m \frac{K_L C_e}{1 + K_L C_e}$ (4) where q_m is the Langmuir constant, which indicates the adsorption capacity of the adsorbent (mg/g), while K_L represents the adsorption affinity

between adsorbate and adsorbent (L/mg). Freundlich equation describes the adsorption behavior of the heterogeneous systems. The

4 Freundlich equation has the following mathematical form

: $q_t = K_F C_e^{1/n}$ (5) where K_F represents the adsorption affinity (mg/g)(mg/L)⁻ⁿ and n is a Freundlich constant which represents the heterogeneity of the system [18]. The fitted

1 parameters of Langmuir and Freundlich models obtained from the fitting of the experimental data are summarized in Table

2, while the plots are given in Fig. 8.

16 As shown in Fig. 8, the amount of adsorbed crystal violet dye molecules is increased along with the increase of

temperature for all systems, indicating that chemisorption is the most dominant process in this adsorption. The increase of temperature helps to increase the adsorption affinity and cause the interaction between adsorbents and dye molecules becomes stronger; thus the adsorption capacity increases. Both adsorption capacity (q_m) and adsorption affinity (K_L), the parameters in Langmuir model, are temperature dependence parameters. In an exothermic adsorption process, the increase in temperature gives a negative impact on these parameters. Meanwhile, in endothermic adsorption, the increase in temperature gives a positive impact on the parameters. As shown in Table 2, the value of q_m and K_L

1 increase with the increase of temperature thus indicate an **endothermic adsorption process**

. Similar to Langmuir

6 model, the parameters K_F and n in Freundlich model are also temperature

dependence. For a physisorption process, the values of K_F and n will decrease as the temperature increases; while in chemisorption, the increase in temperature will give rise to the value of the parameters. In

1 the adsorption of crystal violet onto the AAB, RB, and

RBA composite, the parameter K_F and n increase as the adsorption temperature increases thus supported the chemisorptions process. With the increase of temperature, there is more heat energy available to be converted into kinetic energy and leading to greater interaction between crystal violet dye molecules and surface of adsorbents. Parameter n in Freundlich also represents the heterogeneity of the surface of adsorbent; as the temperature increases, the value of parameter n also increased, this is due to the increase of the system heterogeneity. Based on the data and calculated parameters, both Langmuir and Freundlich

models gave reasonable and consistent values of their parameters. In the AAB system, the data fitting by using Freundlich equation gave better values of R² than that of Langmuir model. The HYBRID and MPSD values also indicate that experimental and calculated data in Freundlich are closer to each other than in Langmuir. Therefore, from this point of view, the Freundlich

4 equation represents the data better than Langmuir the

AAB system.

10 Table 2 Langmuir and Freundlich parameters for the adsorption of crystal violet onto AAB, RB, and RBA composite

**3 Adsorbent T (°C) Langmuir Parameters Freundlich Parameters q_m (mg/g) KL
RL R² † HYBRID § MPSD ‡ KF (mg/g) n R²**

† HYBRID § MPSD ‡ (L/mg) (mg/L)⁻ⁿ AAB 30 141.0932 0.1766 0.00703 0.8752 609.3664 90.3100 46.5350
5.1009 0.9929 25.5953 17.5692 50 156.7306 0.2971 0.00419 0.8971 535.2573 81.6030 55.0873 5.1140
0.9820 78.2889 30.3660 70 176.6300 0.4476 0.00278 0.8706 814.4050 104.4755 64.7932 5.1256 0.9815
145.1187 39.3272 RB 30 191.3284 0.7214 0.00173 0.9338 305.4419 44.6472 74.6830 5.4973 0.9560
408.5259 70.7110 50 199.0631 0.7223 0.00173 0.9379 281.5130 43.3734 78.3167 5.5952 0.9406 563.4575
83.2349 70 270.9195 0.7923 0.00158 0.9220 632.0558 83.2288 103.5830 5.6031 0.8421 1815.4867
155.0829 RBA composite 30 398.5130 0.2320 0.00536 0.9242 687.7220 67.6047 93.7641 3.4687 0.9481
1518.7219 139.3445 50 454.2653 0.2334 0.00533 0.9523 511.6368 63.8123 104.8552 3.4823 0.9247
2225.9307 168.6787 70 476.0389 0.2554 0.00487 0.9144 1206.8137 99.6014 113.0104 3.4847 0.8913
3072.5068 199.7183 †R² is sum squares of residuals between calculated and experimental data; the value
was obtained directly from data fitting by using Sigma plot. §HYBRID = 100 (q_{e,exp} - q_{e,cal})² / n - p ∑
q_{e,exp} (q_{e,exp} - q_{e,cal})² ‡MPSD = 100 1 / ∑ (q_{e,exp} / n - p) with

11 n is the number of the data points and p is the number of parameter within the model

. L. Laysandra et al. / Desalination and Water Treatment 160 (2019) 354–365 The adsorption of violet crystals into RB and RBA composites was found to fit the Langmuir better than the Freundlich equation thus suggesting that the adsorption has a homogeneous surface coverage; the HYBRID and MPSD error functions also resulting in lower values for Langmuir compared to Freundlich.

6 A similar phenomenon also observed in the study by Oladipo et al., the chemisorption of

crystal violet onto A-AAB also found to be fitted well with Langmuir [25]. Brião et al. also found

1 that the adsorption of crystal violet onto

Chitin/ZSM-5 follows Langmuir

5 better than the Freundlich equation [26]. Some comparison **studies** regarding the adsorption of

crystal violet dye onto other adsorbents are summarized in Table 3. The use of rarasaponin to intercalate bentonite is Fig. 8. Adsorption isotherms of crystal violet onto (a) AAB, (b) RB, and (c) RBA composite. Table 3 Comparison study

19 for the adsorption of crystal violet dye onto

various adsorbent Adsorbent‡ HDTMA-bentonite A-AAB Ch-GO/PUF Natural zeolite HDTMA-zeolite CTAB-zeolite Chitin/ZSM-5 AAB RB RBA composite Characteristic Chemisorption Chemisorption Chemisorption Chemisorption Chemisorption Chemisorption Chemisorption T (°C) 30 25 35 40 40 40 25 70 70 70 qm (mg/g) 0.16 (365.11 μmol/g) 582.4 64.935 8.564 13.148 5.539 1217.3 176.6300 270.9195 476.0389 Isotherm model Ref. Freundlich [27] Langmuir [25] Langmuir [32] Freundlich [28] Freundlich [28] Freundlich [28] Langmuir [26] Freundlich This work Langmuir This work Langmuir This work ‡Abbreviations: HDTMA, hexadecyltrimethylammonium; Ch-GO/PUF, chitosan-graphite oxide/polyurethane foam; CTAB, cetyltrimethylammonium bromide; Chitin/ZSM-5, Chitin/Zeolite Socony Mobil-5; A-AAB, alginate/ acid-activated bentonite; AAB, acid-activated bentonite; RB, rarasaponin-bentonite; RBA, rarasaponin-bentonite-alginate. L. Laysandra

14 et al. / **Desalination and Water Treatment 160 (2019)** 354–365 able to

produce adsorbents with higher adsorption capacity than by using other surfactants; RB (in this study) can adsorb crystal violet dye up to 270.92 mg/g meanwhile HDTMA-bentonite only can adsorb 0.16 mg (365.11 μmol) crystal violet per g of adsorbent [27]. Karadag et al. showed that intercalation of HDTMA into another type of clay mineral, namely zeolite, also can increase the adsorption capacity but the intercalation of CTAB is failed to promote the adsorption capacity; where natural zeolite can adsorb 8.564 mg/g, HDTMA-zeolite 13.148 mg/g, and CTAB-zeolite 5.539 mg/g [28]. An excellent adsorption performance was shown by Chitin/ZSM-5 composite [26], from the study by Brião et al., where the Chitin/ZSM-5 composite can adsorb crystal violet dye 2.6 times (1217.3 mg/g) more than the RBA composite (476.04 mg/g) in this study. However, overall the adsorption performance of RBA composite is still comparable to the adsorbents listed in Table 3. 3.5. Adsorption kinetics studies The adsorption kinetics experiments were conducted to understand the mechanism of the adsorption of crystal violet onto AAB, RB, and RBA composite. The pseudo-

8 first-order and pseudo-second-order kinetic **models were** utilized to correlate the experimental data [29]. **The** mathematical expression for **pseudo-first-order**

can be written as [30]: $q_e (1 - \exp(-k't)) = q_t$ (6) and the pseudo-second-order is expressed as [17]: $q_t = (1 + ks(q_{e2} - q_t)^2) / kt$ (7) Fig. 9. Adsorption kinetics of crystal violet onto (a, d) AAB, (b, e) RB, and (c, f) RBA composite. L. Laysandra et al. / **Desalination and Water Treatment 160 (2019)** 354–365 Table 4

1 Pseudo-first and second order reaction **kinetic parameters for** the **adsorption of crystal violet** AAB, RB, and

RBA composite Initial crystal violet conc. (ppm)

24qe,exp (mg/g) Pseudo first order Pseudo second order k' (min⁻¹) qe,cal (mg/g) R2† HYBRID§ MPD‡ ks

191.min⁻¹) (mg/g) R2

† HYBRID§ MPD‡ AAB 600 800 1000 RB 600 800 1000 RBA composite 600 800 1000 58.1913 71.9238 83.7341 59.9536 79.9042 99.9066 0.4831 0.5168 0.5569 0.4942 0.5190 0.5630 62.5557 0.1361 83.3395 0.1681 105.7798 0.1711 57.8862 0.9990 0.4945 2.5595 0.0355 70.9664 0.9963 2.3267 4.9339 0.0291 82.2333 0.9944 3.9674 7.1721 0.0273 59.6220 0.9984 0.6342 2.4268 0.0353 79.4548 0.9982 1.2597 3.5318 0.0287 99.3535 0.9977 2.0002 3.6184 0.0267 60.7381 0.9716 22.6320 80.8577 0.9832 14.3337 102.1644 0.9650 28.7274 19.6453 0.0037 14.0250 0.0035 14.9088 0.0029 58.3945 0.9998 71.6684 0.9993 83.0382 0.9978 60.1485 0.9998 80.1334 0.9998 100.1302 0.9996 63.7010 0.9953 84.3589 0.9996 106.4786 0.9926 0.0804 0.6506 2.3266 0.1804 0.1946 0.3850 4.0941 0.3977 8.2470 1.0738 2.3726 4.3457 1.4978 1.4459 1.6471 6.2156 2.0363 8.1470 †R2 is sum squares of residuals between calculated and experimental data; the value was obtained directly from data fitting by using Sigma plot. §HYBRID = 100 $\sum (q_{t,exp} - q_{t,cal})^2 / n - p$ ‡MPSD = 100 $\frac{1}{n - p} \sum |q_{t,exp} - q_{t,cal}|$ with

11n is the number of the data points and p is the number of parameter within the model

9where qe and qt (mg/g) are the amounts of crystal violet adsorbed at equilibrium and at time t(min), respectively. Parameters k' (min⁻¹) and ks (g mg⁻¹min⁻¹) are the time constant of pseudo-first-order and pseudo-second-order. The adsorption kinetic

plots and fitting by

4using the pseudo-first-order and pseudo-second-order models are depicted in Fig. 9, while the calculated parameters are summarized in Table

4. The kinetic studies were done at three different crystal violet dye concentrations. The value of parameter k' in the pseudo-first-order model increases with an increase in the initial concentration of crystal violet dye; this is because the time

30needed to reach the equilibrium condition is longer as the

initial concentration increases so that the value of k' is smaller [17]. The parameter k' only able to show the rate of adsorption per minutes but cannot show

16 **the amount of crystal violet dye adsorbed** per min- utes. **The**

27 **pseudo-second-order model can give the**

correct prediction on the amount of crystal violet dye adsorbed per minutes from the parameter of time scaling factor k_s . As shown in Table 4, the value of k_s decreases with an increase in the initial concentration, which means that the amount of crystal violet dye adsorbed per minutes decreases with the increasing initial concentration of the dye. The correlation between the empirical calculated data and the

27 **experimental data to pseudo-first-order and pseudo-second-order**

is found to be very good, this indicated by the R^2 values which are close to 1. As can be observed from the HYBRID and MPSD error function, the error

12 **values for the pseudo-second-order model are smaller than that of pseudo-first-order model; so that kinetics adsorption**

data was better fitted to the pseudo-second-order model than the pseudo-first-order model. The pseudo-first-order model was developed based on the assumption that mass transfer (physorption) is more dominant in controlling the adsorption process, while the pseudo-second-order model assumes that chemical adsorption is the rate of determining step [31]. From the experiment of adsorption isotherm, it was found that chemisorption controls the adsorption mechanism; this is also supported by the result from the experiment of adsorption kinetics. In addition, the predicted value of q_e from the pseudo-second-order model is closer to that obtained experimentally (Table 4).

4. Conclusion The new composite, namely RBA composite, has been successfully synthesized from bentonite, natural surfactant (rarasaponin), and natural polymer (sodium alginate). In the formation of RBA composite, the addition of rarasaponin induced intercalation process in the bentonite inter-layer, while the addition of alginate as the natural polymer helps to join the particles of bentonite and rarasaponin. The addition of rarasaponin and alginate helps to increase the surface area of the adsorbent and increases the adsorption capacity. The RBA composite has the adsorption capacity two times higher than RB, and three times higher than the L. Laysandra et al. / Desalination and Water Treatment 160 (2019) 354–365 AAB. The chemisorption was the dominant process that controlling the adsorption for all studied adsorbents. Acknowledgment

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