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3**Biocomposite hydrogel beads from glutaraldehyde-crosslinked phytochemicals in alginate for effective removal of methylene blue**

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2021 Keywords: Alginate bead Red cabbage extract Phytochemicals Adsorption methylene blue Intraparticle diffusion abstract Phytochemicals, i.e., flavonoids, phenolics, and anthocyanin, extracted from red cabbage, were crosslinked with alginate to prepare biocomposite hydrogel beads (BHB). The preparation of BHB involved three consecutive steps: (1) extraction and solvent reduction of phytochemicals from red cabbage, (2) crosslinking of phytochem- icals into alginate matrix using glutaraldehyde, and (3) formation of the hydrogel beads in CaCl2 solution. The resulting BHB sorbents

1**were characterized** using **scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD**) analyses. **The** cross-section structure **of the**

BHB was confirmed from the SEM images. The alteration of FTIR peaks implied the success of the crosslinking of phytochemical com- pounds into the alginate. The adsorption equilibrium and kinetic studies of BHB were conducted using basic blue 9 (BB9) as the model adsorbate. FTIR characterization of the BHB post-adsorption reveals the

25**functional groups of the adsorbent** involved in **the** dye adsorption. **The** calculated adsorption isotherm, kinetics, and thermodynamic parameters show good agreement with the characterization results of adsorbate post-adsorption. The adsorption isotherm is being in congruence with the Langmuir

10**model, and the** highest **adsorption capacity** recorded **was** 1442.0 **mg g**−1 **at** 323 **K**

and pH of 11.0. Adsorption kinetics

4**was better fitted to the** pseudo 1st **order model than the pseudo** 2nd **order**

and Elovich models, which further support the dye physisorption behavior. The initial

10**adsorption rate was influenced by the**

rapid surface adsorption followed by intraparticle diffusion. The thermo- dynamic parameters show the spontaneity of the adsorption, and the adsorption proceeds endothermically. The cost analysis shows the economic feasibility of BHB sorbent production for adsorption applications. © 2021 Elsevier B.V. All rights reserved. 1. Introduction The growth of the textile industry can be beneficial to satisfy the clothing demands of the globally ever-growing population. However, the rapid growth of the textile industry can bring a negative impact to the environment as one of the water contamination sources. The sub- stantial amount of water used in the textile-dyeing process often results in difficulties in managing the wastewater, where over 200 m3 of water is used for the textile dyeing process per day [1]. The discharged waste- water from the dye production, which is rich in dyes and heavy metals, is often directly disposed into the water bodies [2]. Globally, there are ⁎

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(S.P. Santoso). 1 These authors contribute equally. more than 700,000 tons of dyes are produced annually. And, with the current expected Compound Annual Growth Rate of 5.9% and at least 2% of dyes were discharged in the aqueous eluent, it is expected that at least 120,000 tons of dyes leaked to water bodies [3–5]. Among the wide variety of dyes, cationic dyes (e.g., methylene blue) are well known to be the most problematic due to their photo-reactivity, which is destructive to the aquatic biota. Light exposure to methylene blue produces single oxygen, which can cause cell damage and conse- quent cell death [2,6,7]. Various water and wastewater treatment techniques have been de- veloped in the past few decades and are widely applied in industrial- scale applications, including filtration, membrane dialysis, coagulation/ flocculation, ion exchange, precipitation, electrochemical treatment, and adsorption. The combination of these techniques has also been fre- quently used to treat complex wastewater, where adsorption is often employed as the first step before any other techniques. In this regard,

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. the adsorption process offers a number of advantages, including sim- plicity and flexibility in the design and operation, cleaner and harmless effluents post-usage, as well as safe and economical. With respect to dye-contaminated water, adsorption techniques have been widely ap- plied, mainly due to the ease of adjusting the adsorbent binding sites so that dye removal in low concentrations is possible [8–12]. The utilization of sodium alginate (Alg) as a versatile biopolymer has been extensively described in many advanced applications, such as 3D printing, wound dressing, adsorption, and food packaging. In the adsorption technology, a variety of Alg (in its Alg-hydrogel form) was used as an adsorbent for a range of adsorbate-from drug to haz- ardous materials such as heavy metals, organic compounds, and dyes. In addition, various modification strategies of Alg-based hydrogels (HAlg) have been reported in an effort to enhance the ad- sorption capacity. For example, the modifications using clay minerals (e.g., zeolite and bentonite) can promote the adsorption capacity of HAlg [13–15]. This promotion is predictable because the clay minerals are known as super-adsorbents. However, the increase in adsorption results was not as high as expected because the layer of Alg particles blocked most of the surface area of the clay minerals. Nonetheless, the HAlg/clay mineral composite adsorbents have advantages in terms of environmental friendliness, low-cost, and ease of prepara- tion. Fabrication of HAlg using natural bioactive compounds contain- ing oxygen functional groups is another facile method that can promote adsorption ability. In 2012, a study reported the modification of Alg-based hydrogels using humic acid, which may improve its ad- sorption capacity [16]. The incorporation of oxygen-containing func- tional groups, such as hydroxyl, carboxylates, and amine groups, to the HAlg surface is postulated to enhance the adsorption capacity by providing active sites for adsorbate binding. These functional groups can increase adsorption capacity by contributing to the electrostatic interactions, especially toward charged solutes (e.g., cationic dyes, an- ionic dyes, and metal ions). In this study, we attempted to combine the crude plant extract containing bioactive compounds (i.e., phenolic, flavonoids, and alka- loids) with Alg-based hydrogel beads for improved adsorption capac- ity. Red cabbage extract was used as the model since it has been well- known for its high polyphenols content (i.e., anthocyanins, phenolics, and flavonoids). These polyphenols are known to possess various

20**functional groups, such as hydroxyl (OH**), methoxide (OCH3), **and** car- boxyl (**COOH**

) [17]. Incorporating these functional groups onto the Alg matrix can provide additional adsorption sites that lead to the adsorp- tion capacity enhancement.

9**To the best of our knowledge**, our group **is** the first to **report**

an increase in the adsorption capacity of Alg-based adsorbents after being modified with plant crude extract. A single ad- sorption system was studied on the pristine and modified Alg-based hydrogel beads against methylene blue dye (also known as Basic Blue 9, BB9) to investigate the effect of plant crude extract modifica- tion. The effects of several operating parameters (i.e., temperature, solution pH, and contact time) on the adsorption performance of Alg-based composite hydrogel beads were investigated and thor- oughly discussed.

19**2. Materials and methods 2.1. Materials** Red cabbages **were** purchased **from a local** traditional **market**

in Su- rabaya, East Java, Indonesia. Sodium alginate (5.0–40.0 cps in viscosity) was obtained from a local chemical distributor (C.V. Nura Jaya). Techni- cal grade ethanol (96% purity) was purchased from Indofa Utama Multi Core company (Indonesia). Calcium chloride (CaCl2, 98.0% purity), glu- taraldehyde (GA, 25 wt% solution), basic blue 9 (BB9, CI 52015) were obtained from Merck Millipore (Germany). Acetic acid glacial (99.5% purity) was supplied by Sigma-Aldrich (USA). 2.2. Preparation of red cabbage extract (RCE) 3.0 kg of fresh red cabbages (RC) were cut into small pieces and crushed using a blender to obtain RC juice. A 5.0 L of the solvent mixture consisting of 1:1 (v/v) ethanol/water was prepared, followed by acidification to a pH ~3 with acetic acid glacial. The as-prepared solvent was then added to the RC juice, and the mixture was shaken in a shaker bath. The process was conducted in a closed container at room temperature overnight. Subsequently, the RC cake was filtered and the RC ex- tract (RCE) was collected. The RCE solution was then centrifuged at 5000 rpm to remove the remaining cake residue. Afterward, the RCE solution was slowly concentrated by evaporating the solvent at 40 °C using a rotary evaporator until about 1.0 L of viscous solution was ob- tained. The total flavonoid content (TFC), total phenolic content (TPC), and total anthocyanin content (TAnC) of the RCE was determined ac- cording to the previously reported method [18] and the results are found to be: KFC = 590.06 ± 0.81 mg quercetin/L, TPC = 697.52 ± 4.67 mg gallic acid/L, and TAnC = 250.35 ± 2.70 mg L−1. 2.3. Preparation of biocomposite hydrogel beads (BHB) To prepare BHB, 3 wt% of Alg powder was added slowly into 100 mL of RCE. The solution was stirred in a closed glass container for 1 h to ob- tain a homogenous viscous solution. The viscous solution was then dripped into a 3 wt% aqueous CaCl2 solution using a 1000 μL micropi- pette to obtain the hydrogel beads. The obtained beads had an average diameter of 4.5 mm. Subsequently, the resulting beads were immersed into a 1 wt% glutaraldehyde (GA) overnight to crosslink the Alg and the phytochemicals in RCE. The beads were then collected and thoroughly rinsed with distilled water. The beads were kept in a plastic-vacuum bag and stored in the refrigerator before use. In this work, beads were used directly or stored for a maximum of 1 day before use. 2.4. Characterization of the BHB adsorbents The

12**surface functional groups were determined using Fourier** trans- form **infrared** spectroscopy (**FTIR) using a Shimadzu**/FTIR-**8400S** spec- trophotometer. **The** surface morphology **was**

examined by

3**scanning electron microscopy (SEM) analysis** on **a** field-emission **JEOL JSM**

- 6390. The point-of-zero-charge (PZC), which

35**is defined by the point where the curve pHfinal vs. pHinitial crosses the line pHfinal = pHinitial, was** determined according to **the**

previously reported procedure [19]. 2.5. Adsorption study 2.5.1. Preliminary experiments In this work, the BHB sorbent was prepared from the combination of Alg, GA, and RCE (Alg/GA/RCE). A preliminary experiment was con- ducted to assess the adsorption performance of the Alg/GA/RCE with the unmodified Alg and the Alg/RCE beads (without GA crosslinking). Briefly, the unmodified Alg beads were prepared by dissolving 3 wt% of Alg powder in 100 mL distilled water. Meanwhile, the Alg/RCE was prepared by dissolving 3 wt% of Alg powder in 100 mL RCE. The resulting Alg and Alg/RCE hydrogel beads were then obtained by dropping the respective solutions into a 3 wt% of CaCl2 solution. The ob- tained hydrogel beads were then collected and rinsed with distilled water. The adsorption capacity of the three hydrogel bead samples, namely Alg, Alg/RCE, and Alg/GA/RCE was compared. One bead (1.47 ± 0.07 g wet weight and 0.03 ± 0.00 g dry weight) of each sample was added to BB9 solutions at three different concentrations (i.e., 100, 300, and 500 ppm). The adsorption tests were then allowed to run for 8 h at 30 °C to reach an equilibrium. The residual concentrations of BB9 were measured using a spectrophotometric technique in

4**a Shimadzu UV/Vis spectrophotometer at** λmax **of** 663 **nm**

. 2.5.2.

15**Adsorption study The effect of pH on the adsorption**

of BB9 dye on Alg/GA/RCE BHB was evaluated over a pH range from 2

34**to 12 with** an **initial dye** concen- tration **of 100 mg L**−1 and **a**

constant adsorbent mass of 0.03 g. The

4**pH was adjusted using 0.1 N HCl or NaOH solutions** and detected using **the**

Mettler Toledo digital pH meter. The adsorption

37**process was carried out** for 8 h **at room temperature** using **a**

Memmert shaking water bath. The percentage of dye removal (%R) by the adsorbent at each pH condi- tion was calculated according to Eq. (1): %R ¼ ðC0−CeÞ x 100% ð1Þ C0 where C0 and Ce are the concentration of BB9 at initial and equilibrium (mg L−1), respectively. Adsorption isotherm experiments were conducted using

15**25 mL of** BB9 **solution with** various **initial** concentrations **of** 100–2000 **mg L−1**

. A known amount of adsorbent was introduced

32**into a series of conical flasks containing** BB9 **solution**. Subsequently, **the flasks were** placed **in a Memmert shaking water bath** for 8 h **at**

a specific temperature (i.e., 303, 313, and 323 K). The adsorbent was then separated from the BB9 solution by filtration. The equilibrium concentration of BB9 solution after adsorption was quantitatively determined using a

4**Shimadzu UV/ Vis spectrophotometer at a** λmax **of** 663 **nm. The** equilibrium **adsorption**

capacity (Qe, mg g−1)

14**was calculated using the following equation: Qe** ¼ ðC0−CeÞ **V m** ð2Þ **where** m **is the**

mass of adsorbent added into BB9 solution (

1**g) and V is the volume of** the BB9 **solution** in (**L**). The **adsorption** kinetic experiments **were** investigated **at**

three different initial concentrations of BB9 (i.e., 300, 500, 700, and

27**1000 mg L−1). The amount of** BB9 **adsorbed**

was measured at an hour interval until a certain plateau (or no further changes in concentra- tion) was achieved. The amount of BB9 dye adsorbed at a given time (Q t, mg g−1) was calculated according to Eq. (2), with the symbol “e” corresponding to the equilibrium state is replaced by “t”, which refers to the state at a given time. 3. Results and discussion 3.1. Characterization of the BHB adsorbents SEM, FTIR spectroscopy, and XRD characterizations were performed to examine the characteristics of BHB prepared from Alg/GA/RCE and compare to those of unmodified-Alg and Alg/RCE samples. The FTIR spectra showing the functional groups of the adsorbent materials are presented in Fig. 1a. The presence of new absorption bands correspond- ing to the polyphenol compounds of RCE was indicated by asterisks (*), for example the absorption peak at 1512 cm−1 for Alg/RCE and Alg/GA/ RCE samples

37**corresponds to the C–O stretching vibration of the**

methoxy (OCH3) groups. Other peaks corresponding to the polyphenol compounds present in the Alg/RCE and Alg/GA/RCE samples are located at 644 and 677

26**cm−1**, respectively, **which** can **be assigned to the** out-of- **plane bending vibration of**

methyl groups. Furthermore, the presence of GA crosslinking in the Alg/GA/RCE was confirmed by the

2**absorption band at** 1697 **cm−1**, which **corresponds to the** C=O **stretching vibration of the**

aldehyde group. Other characteristic absorption bands of Alg/RCE and Alg/GA/RCE samples are similar to that of Alg, which is reasonable since Alg itself contains identical functional groups with the polyphenols (e.g., –OH and –COOH). The observable characteristic bands are as follows: the free –OH vibration band was indicated by the presence of a broad- spectrum at a wavenumber range of 3600–3200

17**cm−1. The** absorption **band** detected **at** 2901 **cm−1** in unmodified-Alg **indicates**

the aliphatic C–H stretching [20], the dissapearance of this peak in Alg/RCE and Alg/ Fig. 1. (a) FTIR spectra and (b) XRD patterns showing polyguluronate (PG), polymannuronate (PM), and amorphous halo (Am) units for (i) Alg, (ii) Alg/RCE, and (iii) Alg/GA/RCE BHB samples. GA/RCE sample can be attributed to the coordination of this group with the polyphenols of RCE. The

36**stretching vibration of the** C=O **group** was detected **at** 1607 **cm−1 for**

unmodified-Alg, 1611 cm−1 for Alg/RCE, and 1615 cm−1 for Alg/GA/RCE. The anti-symmetric -COO− vibration band was observed for all samples at ~1430 cm−1. The peak observed at ~1030 cm−1 for all samples corresponded to the partial- covalent bonding of Ca and oxygen atom to form the hydrogel beads [20,21]. The presence of guluronate and mannuronate units (the specific units of Alg polymer chain) was indicated by a band at ~810 cm−1 [20,21]. The XRD patterns (Fig. 1b) of the as-prepared hydrogel beads all show the characteristic Bragg reflections associated with the primary units of Alg polymer, namely polyguluronate (PG), polymannuronate (PM), and amorphous halo (Am) units [22]. The peak of the PG unit was observed at 2θ of 13.9°, 14.6°, and 14.1° for unmodified-Alg, Alg/ RCE, and Alg/GA/RCE samples, respectively. The PM unit was observed at 2θ of 22.9°, 21.4°, and 21.8°. And, the Am unit at 2-Theta 38.6, 37.4, and 39.0°. It appears that the crosslinking of RCE to Alg only causes an unnoticeable shifting of the XRD peaks and does not cause the alteration of the XRD pattern. The SEM images of the

3**surface and cross-section** morphologies **of the**

three BHB particles (i.e., Alg, Alg/RCE, and Alg/GA/RCE)

3**are displayed in Fig**. 2. **As can be seen in**

Fig. 2a–c, all three BHB samples ex- hibit a globular shape. Higher magnification images (Fig. 2d–f) reveal that the Alg beads have a smoother surface than those of Alg/RCE and Fig. 2. (a-c) SEM images the whole spherical shape of Alg, Alg/RCE, and Alg/GA/RCE BHB. (d-f) SEM images showing the surface morphology Alg, Alg/RCE, and Alg/GA/RCE BHB. (g-i) SEM images showing the cross-section of Alg, Alg/RCE, and Alg/GA/RCE BHB. Fig. 3. (a) %Removal of BB9 at a different initial concentration (C0) using different Alg-based adsorbent, adsorption was conducted using 0.03 g of the adsorbent for 8 h at 30 °C, and pH of 11. (b) %Removal of BB9 at different pH, adsorption was conducted using 0.03 g of the adsorbent for 8 h at 30 °C, and C0 of 100 mg L−1. The green bar, red bar, and black bar show the properties of Alg, Alg/RCE, and Alg/GA/RCE, respectively. Alg/GA/RCE samples, implying that the incorporation of polyphenols into Alg induces a change in the gelation properties. The change in the gelation properties of Alg can be attributed to the interaction of poly- phenols with the Alg matrix [23,24]. In the Alg/GA/RCE sample, some cavities on the particle surface resembling large macropores are evident (Fig. 2f). The formation of such surface cavities can be ascribed to the presence of polyphenols in the Alg matrix that provides additional func- tional groups (i.e., OH, OCH3, and COOH), which may limit the diffusion of Ca2+ into the Alg matrix [24,25], and thus reduce the gelling ability. The cross-sectional morphology of all three BHB particles is shown in Fig. 2g–i, characterizing the nonporous structure with a crater-like to- pography and relatively smooth surface. 3.1.

9**1. Effect of** pH **and initial** adsorbate **concentration** on **the adsorption of**

BB9 dye The solution pH and the initial adsorbate concentration play impor- tant roles in determining the adsorption performance of an adsorbent [26–28]. Fig. 3a

29**shows the effect of the initial adsorbate concentrations on the** percentage **of**

dye removal by three BHB sorbents. It can be seen that the Alg/GA/RCE exhibits the highest removal efficiency of BB9 at all initial dye concentrations (C0). The removal capacity of the Alg/RCE is also slightly higher than that of pristine Alg. These result sug- gest that the incorporation of RCE-derived polyphenols provides addi- tional adsorption sites to accommodate higher amounts of dye molecules. More importantly, the presence of GA cross-links can aid in strengthening the binding of polyphenol molecules within the hydrogel bead. Without the GA cross-links, these polyphenols are weakly bound to the Alg surface and can be removed easily during the preparation, thus leading to only a marginal increase in the removal efficiency of Alg/RCE compared to that of Alg. Thus, the enhanced adsorption capac- ity of Alg/GA/RCE can be mainly attributed to the cross-linking of RCE by GA, which allows for an increased amount of polyphenols to be strongly bound within the Alg matrix. Furthermore, the higher removal effi- ciency of Alg/GA/RCE can be attributed to the presence of cavities on the surface of the sorbent (as evidenced by the SEM image in Fig. 2f), which may increase the pore volume of the materials and result in supe- rior removal efficiency. Fig. 3b

7**shows the effect of** solution **pH on the removal** performance **of**

BHB samples toward BB9. In this regard, the alkaline pH conditions cause the

16**deprotonation of surface functional groups of the**

BHB adsor- bents, such as hydroxyl (OH) and carboxyl (COOH) groups, thus provid- ing a net

39**negative charge on the surface**. Experimental support for **this** statement **is** provided **by**

the PZC measurement

36**shown in Fig**. 4a. **The** PZC **value of the Alg**

/GA/RCE BHB was found to be 7.7, which implies that the adsorbent bears

4**a negative surface charge at pH** conditions higher than **the** pHPZC. Meanwhile, **the**

BB9 molecules are present in the cationic form at high pH [29]. Accordingly, the different charges be- tween these two species lead to the attractive interaction of BB9

45**dye cations** onto **the negatively charged surface of**

BHB. The magnitude of the negative charge also becomes greater at higher alkaline pH and therefore the removal efficiency of BB9 was higher at pH 11 than that at pH 9.

3**A similar phenomenon was** also observed **in other studies**, in which the **adsorption**

of Alg-based materials becomes more pro- nounced at higher pH values [14,30]. Note that the small difference in removal efficiency between Alg (72.8%) and Alg/RCE (74.2%) at pH 11 could be mainly ascribed to the partial loss of available adsorption sites of the latter due to the enhanced degradation of some polyphenols under such highly alkaline condition [31,32]. Better BB9 removal at al- kaline pH could also be related to the swelling ability of BHB sorbent. Immense particle swelling occurs at a more alkaline pH, which is due to the chain expansion induced by the presence of deprotonated car- boxyl groups on the Alg backbone [33]. More significant particle swell- ing at pH 11 (Fig. 4b) could afford more contact areas on the surface of BHB, thus allowing an enhanced electrostatic interaction with cationic BB9 molecules. Fig. 4. (a) The point-of-zero-charge (PZC) value of Alg/GA/RCE BHB. (b) Swelling diameter (Ø) of the Alg/GA/RCE BHB after adsorption of BB9 at different pH conditions. 3.2. Adsorption mechanism of BB9 onto BHB The FTIR spectra of pristine and BB9 loaded-BHB adsorbents are re- corded to elucidate the dye adsorption mechanism. As shown in Fig. 5a, several distinct spectral features were observed after dye sorp- tion, as highlighted by the four blue regions. In the highlighted area (i), the shape and intensity of the peak corresponding to the free OH group are altered significantly. This suggests that the surface hydroxyl group plays an active role in the adsorption of BB9. In region (ii), the

9**band at** 1615 **cm−1 corresponding to the**

carboxyl group was altered in shape and shifted to 1623 cm−1, which suggests an interaction be- tween BB9 and the C=O group of the adsorbent. The

9**vibration band of the** group **at** 1030 **cm−1**, at **the**

area (iii), was still observed in the spec- tra before and after dye adsorption. However, the band shape was dif- fering significantly; this can be due to the inclusion of BB9 molecules in the internal structure of the crosslinked group of the adsorbent. In the blue area (iv), new peaks are observed in the spectral of adsorbent post-adsorption. The peaks could be attributed to the C–Cl vibration bands originating from the Cl− ions of BB9. The Cl- ions may also be adsorbed from the bulk solution

9**during the adsorption process. The** XRD pattern **of the** BHB post-**adsorption**

is presented in Fig. 5b. It can be shown that there is no apparent change observed in the XRD pat- terns of the adsorbent before and after dye adsorption. This result sug- gests that no structural alteration of the adsorbent and physisorption plays a dominant role in the dye uptake. 3.3. Adsorption isotherm An adsorption isotherm study of BB9 on three BHB samples was con- ducted to gain insight into the adsorption behavior. The classical two- parameter models, namely

31**Langmuir and Freundlich, were applied to** correlate **equilibrium adsorption** data **and**

predict the homogeneity of adsorbate distribution on the adsorbent surface area. The Langmuir iso- therm model was developed based on the assumption of monolayer Fig. 5. (a) FTIR spectra and (b) XRD patterns of BHB before and after the adsorption process of BB9. The blue-highlighted areas in FTIR spectra show the apparent alteration in the spectral features of BHB post-adsorption of BB9 dye. formation of adsorbate molecules on a homogeneous surface [34]. The nonlinear mathematical model of Langmuir is expressed as follows: Qe ¼ Q1L,þmaKxLKCLeCe ð3Þ

3**where Q L,max is the theoretical maximum**

5**adsorption capacity (mg g−1), KL is** a fit parameter **related to the affinity** between **the** adsorbent and the **adsorbate (L mg−1**), and Qe represents **the**

equilibrium adsorption capacity (mg g−1). Meanwhile, the

17**Freundlich model was** established based **on the** multilayer adsorption **assumption** over **the** heterogeneous **solid surface**

[35]. The

1**mathematical expression of Freundlich is given** in **Eq**

. (4): Qe ¼ KFCe1=nF ð4Þ

5**where KF is the Freundlich** adsorption **constant ((mg g−1)(mg L−1)-n), and** nF **is the** Freundlich exponent coefficient. **The**

value of 1/nF

22**can be used to predict the** favourability **of the adsorption process**, that **is**

when 1/nF < 1. Three-parameter isotherm model was also applied for fitting equi- librium data, which is the Redlich-Peterson model. The Redlich- Peterson model represents a combination of Langmuir and Freundlich isotherms for predicting the homogeneous approach

40**to the surface area of the adsorbent** [36]. **The** hyperbolic model of the Redlich- Peterson isotherm is given in Eq. (5): Qe ¼ 1 þABRRPPCCeβeRP ð5Þ where ARP and BRP are the Redlich-Peterson isotherm parameters with the unit of

5**L g−1 and L mg−1, respectively**. The exponential coefficient **β**

RP usually has a value in the range of 0 to 1, which provides the predic- tion of the homogeneity of the adsorbate. The plots showing the adsorption isotherms of BB9 on Alg, Alg/RCE, and Alg/GA/RCE

15**at different temperatures** are given **in Fig. 6**. In **all** cases, **the**

isotherm plots reflect

16**an L-curve subclass 2 according to** the classifi- cation **by Giles et al**

. The L-curve is often observed for the solute adsorp- tion in an aqueous solution where the adsorption process proceeds until the number of adsorption sites becomes depleted, and the adsorbent is finally saturated with solute molecules. In addition, the plateau in the adsorption system belonging to subclass 2 occurs due to the adsorbent monolayer saturation. Thus, it also implies that the adsorbents with a higher number of adsorption sites possess a greater adsorption capacity. This premise is reasonable to explain the higher adsorption capacity of Alg/GA/RCE than Alg and Alg/RCE. The higher number of adsorption sites in the Alg/GA/RCE surface can be attributed to the crosslinking of the polyphenols in the Alg matrix by GA. The fitted parameters of the BB9 equilibrium adsorption data using Langmuir, Freundlich, and Redlich-Peterson models are presented in Table 1. The Langmuir and Redlich-Peterson models seem to fit the ad- sorption data better than the Freundlich model, judging from the corre- lation coefficient R2 (which is close to 1) and the low

10**root-mean-square error (RMSE) values. The**

43**Redlich-Peterson is a hybrid model** of Lang- muir **and Freundlich**

, where the value of βRP parameter can describe the tendency of the adsorption system. As the value of βRP close to 0, a heterogeneous adsorption system is obtained as the Redlich-Peterson equation is reduced to the Freundlich equation. On the contrary, as β RP close to 1, this equation is reduced to Langmuir, and thereby homo- geneous adsorption behavior is expected. Table 1 shows that the βRP value is close to 1 for almost all systems, implying that the adsorption approaches the

13**Langmuir model. The fitting** results are also **consistent with the previous classification by Giles** et al., **where most**

of the adsorp- tion systems with an L-curve

13**are well-convergence with the Langmuir model fitting** [37]. **The** satisfactory

1**fitting of** the **adsorption data to the Langmuir**

model is also an indicative that the

22**dye molecules** are **adsorbed** flat **on the surface of the** adsorbent. **The adsorption process**

of BB9 onto the BHB particles seems to be temperature-dependent. A higher adsorption capacity is achieved at el- evated temperatures of the system. This phenomenon can be explained by the solubility nature of the solute dye molecules (i.e., BB9). The solu- bility of the adsorbate will be higher as the temperature increases, thus facilitating its mobility toward the adsorbent matrix. Moreover, an in- crease in temperature may also induce a greater swelling degree of the BHB, which could promote the pore enlargement of the adsorbent and facilitate the

45**diffusion of the dye molecules** into **the** adsorption sites. **The** fit parameter **of**

the Langmuir model, that is Q L,max, shows that Alg/GA/RCE has the highest monolayer adsorption capacity than Alg and Alg/RCE across all temperatures; suggesting that the crosslinking of RCE polyphenols

1**into the** Alg **matrix resulted in** the significant **improvement in the adsorption**

capacity. This perfor- mance improvement can be attributed to the presence of RCE poly- phenols that provide additional

34**adsorption sites for cationic dye molecules in** the form **of**

20**functional groups such as –OH**, –OCH3, **and –COOH. The**

as-prepared Alg/GA/RCE also shows superior adsorption capacity toward BB9 compared to other previously reported alginate-based composite adsorbents, as listed in Table 2. It is worth noting that Alg/GA/RCE possesses higher adsorption ca- pacity toward BB9 than the mentioned Alg-based adsorbents and the common adsorbents (i.e., activated carbon and clay mineral). However, in a recyclability test attempt, the BHB particles broke after the first reuse experiment due to excessive swelling, thus indi- cating that this adsorbent is unlikely to be recycled. However, BHB offers several advantages, such as high adsorption capacity, low Fig. 6. Adsorption isotherm data at different temperatures and the nonlinear fittings using Langmuir, Freundlich, and Redlich-Peterson models. cost, and ease of preparation. Also, BHB is prepared from non-toxic, naturally abundant, and environmentally benign materials, which are expected not to cause environmental damage when disposed-of. 3.4. Adsorption kinetics The adsorption kinetics of BB9 onto BHB (i.e., Alg/, Alg/RCE, and Alg/ GA/RCE) were studied at the optimal pH of 11 and

4**30 °C. The adsorption** kinetics **data were**

interpreted using the pseudo 1st

5**order, pseudo** 2nd **order, and Elovich** model. **The nonlinear** mathematical equations for **pseudo** 1st **order and pseudo** 2nd **order**

are presented in Eqs. (6) and (7), respectively [46]. Q t Q 1 1−e−k1 t ¼ ð6Þ Q t ¼ 1 kþ2 kQ22Q 2 t 2 t ð7Þ

27**where Qt (mg g−1**) represents **the amount of** BB9 adsorbed **at** a specified **time t**

(h). Q1 (

44**mg g−1) and** Q2 (**mg g−1) are the** estimated equilibrium **amount of** BB9 **adsorbed** for pseudo 1st **and pseudo** 2nd **order rate**

equations,

11**respectively. The** parameter **k1** (h−**1) and k2 (g mg−1** h−**1) are the** corresponding apparent sorption **rate** constant **of pseudo** 1st **and pseudo** 2nd kinetic **models, respectively**

. Table 1 Adsorption isotherm parameters

31**for the adsorption of** BB9 **on** BHB (**Alg, Alg**/RCE, **and Alg**

/ GA/RCE) at different temperatures. Model Parameter Alg Alg/RCE Alg/GA/RCE Adsorption at T = 303 K Langmuir QL,max (

8**mg g−1) KL (L mg−1**) R2 RMSE **Freundlich** KF (**mg g−1) (mg L−1)1**/n **nF**

R2 RMSE Redlich-Peterson QRP (

19**mg g−1) β** RP **R2 RMSE**

Adsorption at T = 313 K Langmuir QL,max (

8**mg g−1) KL (L mg−1**) R2 RMSE **Freundlich** KF (**mg g−1) (mg L−1)1**/n **nF**

R2 RMSE Redlich-Peterson QRP (mg g−1) βRP R2 RMSE Adsorption at T = 323 K Langmuir QL,max (

8**mg g−1) KL (L mg−1**) R2 RMSE **Freundlich** KF (**mg g−1) (mg L−1)1**/n **nF**

R2 RMSE Redlich-Peterson QRP (

19**mg g−1) β** RP **R2 RMSE**

725 0.02 0.99 19.31 54.28 0.45 0.97 41.69 809 1.00 0.99 20.48 886 0.03 1.00 7.13 96.54 0.39 0.96 57.90 1084 1.03 1.00 6.62 840 0.02 1.00 12.86 82.34 0.40 0.97 12.86 923 1.05 1.00 12.87 921 0.03 0.98 37.47 151.75 0.31 0.90 94.31 1206 1.22 0.99 23.55 1055 0.021 0.98 29.54 92.78 0.34 0.89 46.40 968 1.02 0.99 22.60 1169 0.02 0.98 50.61 141.41 0.36 0.91 112.62 1261 1.16 0.98 44.82 1389 0.02 0.92 31.85 184.34 0.3525 0.80 48.48 1418 1.11 0.95 62.57 1400 0.03 0.95 45.68 180.73 0.37 0.84 54.84 1489 1.13 0.98 49.00 1442 0.03 0.99 23.19 123.39 0.45 0.92 47.59 1567 1.17 1.00 28.50 The Elovich model is postulated to suit the chemical adsorption sys- tems with heterogeneous adsorbent surfaces, which has the following expression: Qt ¼ lnð1þαβtÞ 1 β ð8Þ where

33**α (mg g−1** h−**1) is the initial adsorption rate** and **β (g mg−1) is the desorption constant**

. An equilibrium constant (RE) representing the adsorption characteristic can be calculated from the Elovich param- eters: RE ¼ 1=Q ref β ð9Þ with Qref

6**is the adsorption capacity** obtained **at t** = tref **and** tref **is the**

lon- gest time in adsorption process. The adsorption characteristics based on RE can be classified as follows: slow rising when

47**RE > 0.3**, mild **rising** for **0.3 > RE > 0.1**, rapid **rising** for **0.1 > RE > 0.02**

, and instantaneous ap- proaching equilibrium when RE < 0.02 [47,48]. The fitting of the

1**kinetic models to** the **experimental data is** pre- sented **in Fig**. 7, while **the**

values of the fit parameters are given in Table 3. Among the three investigated kinetic equations, the pseudo 1st order

6**was the most suitable model to** fit **the data** points for BB9 **adsorption**

by BHB (Alg, Alg/RCE, and Alg/GA/RCE). This suitability can be observed from the correlation factor values (R2) of the Pseudo 1st order, which approach unity. Also, the low RMSE of the Pseudo 1st order further confirms the suitability of the model. When an adsorption Table 2 Maximum adsorption capacity of BB9 on several Alg-based composite adsorbents. Adsorbenta QL,max (mg g−1) Ref GO/Alg PVA/Alg/Chitosan/Mont

TA/PVA/Alg Alg/Rice husk GO-Mont/ Alg Hectorite/Alg Activated carbon (from Camellia sinensis L.) Activated clay minerals Biocomposite Hydrogel Beads (Alg/GA/RCE) 357.14 137.15 147.09 344.00 150.66 785.45 324.7 500 1442 [38] [39] [40] [41] [42] [43] [44] [45] This work a GO = graphene oxide, Alg = sodium alginate, PVA = poly(vinyl alcohol), Mont = montmorillonite, TA = tannic acid. system fits the Pseudo 1st order, it can be implied that the rate con- stant (k1) of the system is dependent on the initial concentration of the solute (C0) [46]. As shown in Table 3, the dependency of k1 to C0 can be clearly observed from the difference of k1 values for each system with different C0.

2**Furthermore, it can be** observed **that while the values of Qt** increase **with increasing** C0, k1 decreased **with**

increasing C0. This can be related to the relation between the mass transfer driving force and C0. At high C0, the high number of solute molecules cause an increased mass trans- fer rate toward the adsorbent surface; thus providing a larger

2**driving force for the solute to** overcome **the** adsorbent **boundary layer**

, and con- sequently a higher number of

2**solute molecules** can **be adsorbed**. How- ever, **a** high **number of solute molecules** also cause **the external surface** vacant **sites** of **the**

adsorbent are quickly occupied and thus slow down the

2**diffusion rate of the remaining solute molecules in the bulk solution**

[46,49]. Once

2**all of the surface sites** are **occupied, the**

next adsorption step occurs through the diffusion of the solute mole- cules into the interior porous adsorbent matrix [49]. Fig. 7 also shows the gradual increase in Qt over a prolonged time until it reaches a plateau condition. In the first couple of hours (~3 h), a rapid increase in Qt was observed, and subsequently there is no signif- icant increase in Qt after 3 h.

46**This phenomenon can be** directly attrib- uted **to the high availability of vacant adsorption sites** at **the** initial **stage**. With prolonged **adsorption**

time, the vacant sites become gradu- ally occupied and finally saturated with the solute molecules, thus lead- ing to the saturation of Qt [50]. By comparing the three investigated BHB sorbents, Alg/GA/RCE dis- plays the highest adsorption capacity (Q1) than Alg/RCE and Alg. This re- sult indicates the promoting effect of the RCE addition to the adsorption capacity of the Alg. Interestingly, although the amount of BB9 adsorbed on Alg was lower than Alg/GA/RCE, the adsorption rate (k1) was slightly higher for Alg. This may be attributed to the higher number of adsorp- tion sites in Alg/GA/RCE; thus, a longer time is needed to occupy all of the available sites. Although the kinetic data

29**can be well described by the Pseudo** 1st **model**

, it is still interesting to examine the fit parameters from other models. The calculated parameters Q2 in the Pseudo 2nd order model shows higher values for Alg/GA/RCE than Alg/RCE and Alg, which dis- play good consistency with the Q1 parameter of the Pseudo 1st order. The fitting of the kinetic data using the Elovich model shows lower con- gruency than other fitting models. This may suggest that the chemisorp- tion is not dominant in this process. Furthermore, as shown from the α value, the initial adsorption rate was higher at higher initial adsorbate concentrations, which implies that higher adsorbate concentrations provide a greater mass transfer driving force for the adsorption. Mean- while, desorption of the adsorbate was higher at a lower concentration, as reflected by the high β value. Based on the RE value, a slow rising characteristic was observed at high C0, and it altered to mild-rapid rising characteristics at low C0. This result is in accordance with the adsorption rate constants k1 and k2, which show lower values with increasing C0 parameter. Fig. 7. Adsorption kinetics of BB9 on BHB at various initial concentrations, and the kinetic data fitting using

10**Pseudo 1st order, Pseudo 2nd order**, and Elovich **model**. 3.5. **Intraparticle diffusion** (IPD) behavior **The**

initial rapid adsorption behavior of the BB9 on BHB was further analyzed by fitting the kinetic data using the IPD model. The IPD equa- tion can be expressed as follows: Qt ¼ kIPDt1=2 þ Ci ð10Þ where kIPD (

14**mg g−1 h-1/2**

)

25**is the intraparticle diffusion rate constant and Ci** (mg g−1) **is the** arbitrary constant. **The** Ci **value** is postulated **to**

be closely related to the boundary layer effect, where the greater the value, the greater the boundary. The IPD model has three forms according to the method of data fitting: (1) by fitting

24**a straight line that is forced to pass through the origin**

, (2) by fitting two or three segments straight line, which is known as a multi-linearity plot, and (3) by fitting

24**a straight line that is** not necessarily **pass through the origin**

[46,49,50]. The kinetic data fitting using the single straight line of the IPD model re- sults in a poor R2 value (<0.90), which implies the inadequacy of this fitting approach to interpret the kinetic data. Thus, the multi-linearity approach is applied for the data fitting [51]. The IPD fitting onto the adsorption kinetics data of BB9 on three BHB adsorbents can be divided into two segments for all C0 variants. The first segment ranged from 1 to 4 h (1 to 2 h1/2) of contact time, and the second segment ranged from 4 to 8 h (2 to 2.83 h1/2) of contact time (See Fig. 8). The first segment corresponds to the instantaneous (rapid) surface adsorption, which is confirmed by the high diffusion rate kIPD,1. The second segment can be assigned to the gradual adsorp- tion step where intraparticle (or pore) diffusion occurs; thus, this seg- ment has a lower rate constant (kIPD,2). The lower values of kIPD,2 could also be ascribed to the larger boundary layer effect (see Table 4), which is larger for the second segment compared to the first segment (Ci,2 > Ci,1) [51,52].

1**A similar result was obtained** in the study **by** Tiwari **et al**. (2016), where **the**

adsorption system of lead by the com- posite of Alg/magnetite nanoparticles/bacterial strain followed the two- segment IPD characteristic [53]. 3.6.

30**Thermodynamic evaluation Thermodynamic parameters of** adsorption, **such as** the **Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS**

), are the relevant parameters describing the

26**spontaneity and the** charac- teristic **of the adsorption process** [54]. **The thermodynamic**

parameters at a constant temperature and pressure are calculated according to the following equations: ΔG ¼ ΔH–T:ΔS ð11Þ Table 3 Adsorption kinetics parameters for the adsorption of BB9 on BHB. Model C0 (mg L−1) Alg 300 500 700 1000 Alg/RCE 300 500 700 1000 Alg/GA/RCE 300 500 700 1000 Pseudo 1st order Q1 (mg g−1) k1 (h−1) R2 RMSE 168 1.09 0.99 6.86 383 1.01 1.00 3.51 439 0.74 1.00 11.00 590 0.71 1.00 5.76 164 0.87 1.00 2.39 345 0.85 1.00 7.64 470 0.77 1.00 3.19 674 0.60 0.99 15.96 226 0.84 1.00 4.11 416 0.82 1.00 6.39 595 0.73 1.00 5.72 803 0.71 1.00 1.05 Pseudo 2nd order Q2 (

14**mg g−1) k2 (g mg−1 h−1) R2**

RMSE 200 0.004 0.97 10.69 372 0.004 1.00 7.38 518 0.002 0.98 22.17 696 0.001 1.00 14.09 186 0.004 0.99 5.18 437 0.003 1.00 6.63 617 0.001 1.00 10.45 667 0.002 0.98 27.01 261 0.004 0.98 11.82 466 0.003 0.99 19.34 684 0.002 0.99 20.62 944 0.001 1.00 7.32

28**Elovich α (mg g−1** h−**1) β (g mg−1**) RE **R2**

RMSE 875 0.023 0.16 0.94 14.01 968 0.018 0.17 0.98 14.36 970 0.010 0.24 0.96 31.51 1415 0.007 0.34 0.98 26.25 914 0.031 0.19 0.98 8.50 913 0.009 0.33 0.99 9.79 1033 0.008 0.29 0.99 19.26 1791 0.008 0.33 0.96 37.91 968 0.021 0.06 0.95 17.84 1767 0.014 0.12 0.98 20.82 1784 0.008 0.30 0.97 31.92 2003 0.005 0.58 0.98 37.54 Fig. 8. Adsorption kinetics of BB9 on BHB at various initial concentrations and the data fitting using the intraparticle diffusion (IPD) model. Table 4 Calculated IPD parameters for the adsorption of BB9 on BHB. C0 (

23**mg L−1**) kIPD,1 (**mg g−1** h-**1/2**) Ci,1 (**mg g−1) R2** RMSE kIPD,2 (**mg g−1** h-**1/2**) Ci,2 (**mg g−1) R2**

RMSE Alg 300 500 700 1000 91.76 114.74 218.73 259.92 11.06 107.58 97.19 257.43 0.93 0.94 0.93 0.96 13.58 15.15 32.39 28.15 3.76 10.76 12.66 54.80 153.91 305.88 397.44 442.62 0.87 0.82 0.80 0.99 0.55 1.91 3.21 1.64 Alg/RCE 300 500 700 1000 66.06 147.45 214.17 271.93 34.46 93.93 102.89 139.47 0.96 0.99 0.98 0.96 7.19 8.55 16.90 28.29 4.91 5.23 5.82 54.34 150.31 186.65 325.92 552.19 0.88 0.92 0.85 0.98 0.70 6.11 8.09 0.22 Alg/GA/RCE 300 500 700 1000 101.32 151.66 251.68 351.73 28.46 121.05 97.65 81.87 0.90 0.97 0.94 0.96 28.55 20.93 25.02 38.46 4.96 7.93 14.83 64.40 210.66 394.11 551.60 627.95 0.94 0.92 0.97 0.96 0.74 0.87 1.48 4.78 ΔG ¼ −RT ln K ð12Þ where ΔG represents the Gibbs

17**free energy (kJ mol−1) and** K **is the** equilibrium **constant**

, which can also be related to the equilibrium ad- sorption capacity expressed as ln(Qe/

11**Ce); R is the universal gas constant (8.314 J mol−1 K−1**

). Thus, Eq. (11) can be rearranged to the following expression: ln Qe¼−ΔH ΔS þ Ce RT R ð13Þ The

28**values of ΔH and ΔS can be** obtained as **the**

38**slope and intercept of** the **Van't Hoff** plot **ln**(Qe/Ce) **vs. 1/T, respectively. The** calculated thermo- dynamic **parameters are** given **in Table**

5. As can be seen

21**in Table 5, the negative values of ΔG indicate that the adsorption**

proceeds spontaneously. Also, the more

39**negative values of ΔG** imply **that the adsorption is** more **spontaneous**

at higher tempera- tures. Meanwhile, the positive value of ΔH reflects an endothermic na- ture of the adsorption process, and thus, adsorption is more favorable at high temperatures. Moreover, the ΔH value of <20 kJ mol−1 suggests that physisorption is more dominant in the BB9 uptake process onto BHB and that the adsorption occurs mainly due to the van der Waals forces [37]. The

21**positive value of ΔS° suggests increased randomness at the solid**-liquid **interface**

, leading to decreased solution viscosity. The decrease in viscosity allows an increase in the mass transfer driving force of the solute molecules, which facilitates adsorption. 3.7. Cost analysis The preliminary analysis of the direct operating cost (DOC) was con- ducted to estimate the production cost of the Alg/GA/RCE hydrogel beads. In this context, the production of Alg/GA/RCE only involved a mixing process of all precursor materials and did not require any com- plicated procedure and a large number of workers. Therefore, the DOC analysis of the production of Alg/GA/RCE is calculated based on the costs of the raw materials, and the contribution of utility and operating

43**Table 5 Thermodynamic parameters of the** BB9 **adsorption on**

BHB sorbents.

42**T (K) ΔG (kJ mol^{-1}) ΔH (kJ mol^{-1}) ΔS (kJ mol^{-1} K^{-1}**

) Alg 303 313 323 Alg/RCE 303 313 323 Alg/GA/RCE 303 313 323 −1.9124 −2.2283 −2.6589 −2.4536 −3.0193 −3.9661 −3.3627 −3.8902 −4.5255 9.4163 0.0373 16.524 0.0756 18.7539 0.0729 Table 6 Estimation of DOC for the synthesis of Alg/GA/RCE on the kilogram scale. DOC Specification Price (US$ kg^{-1})a Amount (kg)b Total (US$) Alg $CaCl_2$ GA H_2O Ethanol Acetic acid Red cabbage Total DOC Mw 10,000–600,000 Flakes, 74% 50% 18.2 MΩ Min. 96% Glacial, 99.5% – 4.00 0.12 10.0 0.05 0.95 0.41 0.12 0.06 0.03 0.004 3.0 2.5 0.004 3.0 0.240 0.041 0.040 0.150 2.375 0.002 0.360 3.170 a The raw materials price was based on the China trading price listed by Focus Tech- nology Co. Ltd. b The amount of the raw materials was scaled up on the basis of one kilogram of dried beads production. The estimated amount of water includes water requirements in the beads production process and the washing step. labor costs can be neglected. The price of the raw materials along with their price quotes in US$ are presented in Table 6. The production of Alg/GA/RCE costs only US$3.17 per kg, which is comparable to or even cheaper than other commercial adsorbent materials such as activated carbons (US$0.75–2.60 per kg), bentonite clays (US$0.5–2.2 per kg), sil- ica gels (US$4.4–5.3 per kg), and polymer beads (US$5.5 per kg). Fur- thermore,

13**it is worth mentioning that the adsorption capacity of**

Alg/ GA/RCE hydrogel beads is superior to those of activated carbons and clay minerals (see Table 2), thus implying the application potential of this low-cost alternative adsorbent for dye wastewater treatment. 4. Conclusions The present study demonstrates a facile and green approach for en- hancing the adsorption capacity of Alg-based hydrogel adsorbent by crosslinking phytochemicals (i.e., phenolics, anthocyanin, and flavo- noids) from RCE using glutaraldehyde. The resulting Alg/GA/RCE BHB exhibits a maximum adsorption capacity of 1442 mg g^{-1} toward BB9 dye cations, which is higher than other Alg-based composite adsor- bents. The adsorption study shows that the adsorption was dominated by physisorption, and the adsorption occurs

20**due to the van der Waals interaction. The**

rapid and instantaneous adsorption occurred at the be- ginning of the process and continued by the intraparticle diffusion pro- cess. The adsorption isotherm and kinetics parameters show good agreement with the thermodynamic parameters. In summary, the as- prepared Alg/GA/RCE BHB can be potentially employed as a single-use adsorbent to purify dye-contaminated wastewater with excellent ad- sorption performance.

6**Declaration of Competing Interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to** influ- ence **the work reported in this paper. Acknowledgements The authors gratefully acknowledge** financial support **from the**

16**Widya Mandala** Surabaya **Catholic University through Internal Research Grant. References**

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