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Environmental Science and Pollution Research (2019) 26:22979–22989 https://doi.org/10.1007/s11356-019-05524-0 RESEARCH ARTICLE An environment-friendly composite as an adsorbent for removal Cu (II) ions Livy Laysandra 1,2 & Immanuel Joseph Ondang 1 &

2**Yi-Hsu Ju** 3 &**Jindrayani Nyoo Putro** 2 &**Shella Permatasari Santoso** 1,2 &**Felycia Edi**

Soetarejo 1,2 & Suryadi Ismadji

191,2 **Received**: 27 **February 2019 / Accepted**: 17 May **2019 / Published online**: 10 June **2019 # Springer-Verlag GmbH Germany, part of Springer Nature 2019**

Abstract The

low-cost composite film was prepared by incorporating chitosan, berry soap fruit extract (rarasaponin), and bentonite as the raw materials. The produced chitosan/rarasaponin/bentonite (CRB) composite exhibits outstanding adsorption capability toward copper metal ions (Cu(II)). A series of static adsorption experiments were carried out to determine the isotherm and kinetic properties of CRB composite in the adsorption process. The adsorption equilibrium shows a good fit with the Langmuir isotherm model; the CRB composite has maximum uptake of Cu (II) of 412.70 mg/g; the kinetic adsorption data exhibit a good fit with the pseudo-second-order model. The thermodynamic parameters, ΔH°, ΔG°, and ΔS°, obtained from the isotherm data indicate that the uptake of copper ions by CRB composite is more favored at low temperatures. This study shows that physicochemical modified adsorbent, namely CRB composite, can remove Cu (II) better than pristine adsorbent of AAB and chitosan. The CRB composite also shows potential reusability. Keywords Ca-bentonite . Rarasaponin . Chitosan . Heavy metals . Copper ions . Isotherms . Kinetics . Thermodynamics . Adsorption Introduction Copper metal ions (Cu(II)) are one of the heavy metals most often found as water pollutants. The main source of Cu(II) pollutants mainly comes from wastewater from industries

1**Responsible editor: Tito Roberto Cadaval Jr Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11356**-019-05524-0) **contains supplementary material, which is available to authorized users. * Felycia Edi** Soetarejo **felyciae@yahoo.com * Suryadi Ismadji suryadiismadji@yahoo.com**

1 2 Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia Department of Chemical Engineering, National Taiwan University of Science and Technology, No. 43, Sec 4, Keelung Rd, Da'an District, Taipei City 106, Taiwan 3 Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, No. 43, Sec 4, Keelung Rd, Da'an District, Taipei City 106, Taiwan such as paper, textile, metal alloy, electroplating, and fertilizer (Li and Bai 2005). The presence of Cu(II) in the aquatic en- vironment is a serious problem that requires more attention; this is due to its toxicity to humans and aquatic biota. Although Cu(II) is known as an essential nutrient for normal growth and metabolism, however, the excess amount of this metal can provoke various health disorders (Santore et al. 2001). Exposure of Cu(II) into the human body can occur both through the respiratory and digestive tracts. Accumulation of Cu(II) in the liver can cause mild disorders such as nausea, vomiting, abdominal, and muscle pain, to severe disorders such as gastrointestinal irritation, kidney damage, and liver damage (Liu et al. 2002). At present, there are several methods available to control Cu (II)

14**contamination in water** and wastewater **including chemical precipitation, electrochemical treatment, membrane**

filtration, electrodialysis, and adsorption. Hua et al. (2017) show that chemical precipitation method by using mechani- cally activated $CaCO_3$ can reduce Cu(II) in the water with a removal efficiency of 99.76% (Hua et al. 2017). Electrochemical treatment can reduce Cu(II) concentration in the pickling solution to below 100 mg/L (Karakaya et al. 2018). A recent study by Kontoudakis et al. (2018) showed that membrane filtration using polyethersulfonate and nylon membranes was able to remove sulfide-bound Cu in wine up to 40–90% (Kontoudakis et al. 2018). A Cu(II) removal per- centage of 94.94–97.33% can be achieved by electrodialysis method using a cell packed with a pair of ion-exchange mem- branes and platinum electrodes (Mohammadi et al. 2004). Among the available methods, adsorption is the most pre- ferred because of several appeals including ease of operation, favorable economic aspects, absence of the use of non-environmentally friendly chemicals, and absence of side waste or contaminants. The benefit level of the adsorption depends entirely on the performance of the adsorbent. Adsorbents that have advan- tages such as high adsorption capacity, easy to use, inexpen- sive, harmless, and possible to reuse are still extensively de- veloped today. For this purpose, many research focus on find- ing sophisticated composite materials that show great adsorp- tion capabilities. A recent study by Torres-Caban et al. (2019) shows that composite beads adsorbent made from calcium- alginate/spent-coffee-grounds can adsorb 20.921 mg Cu(II)/ g adsorbent (Torres-Caban et al. 2019). The carbon nanotubes/ polypyrrole composite proposed in the study by Nyairo et al. (2018) have a maximum adsorption capacity of 24.39 toward Cu(II) (Nyairo et al. 2018). Zhou et al. (2017) show that the nano-MnO_2-biochar composite has

31**a maximum adsorption capacity of** 142.02 **mg/g** towards **Cu(II**

) (Zhou et al. 2017). In this paper, a low-cost composite film prepared by combin- ing chitosan/rarasaponin/bentonite is introduced; a consider- able adsorption capability of the composite against Cu(II) is also shown. The new adsorption method specifically emphasizes the use of biomolecules as an adsorbent to treat wastewater; this is because these materials are more environmentally friendly, non-toxic, viable, biodegradable, and capable to interact chemically or physically with various substances (Kurita 1998; Sankararamakrishnan and Sanghi 2006). One of the abundantly available biomolecules is chitosan. Chitosan has extraordinary characteristics such as hydrophobicity, biocom- patible, biodegradable, antibacterial, non-toxic, and high me- chanical strength (Inoue et al. 1999; Cervera et al. 2004). The hydroxyl (–OH) and amino (–NH2) groups of chitosan are the main keys to chitosan modification. Modification of those functional groups allows chitosan to be formed into various forms such as film, fiber, hydrogel, membrane, nanoparticle, and microsphere (Nunthanid et al. 2001; Merrifield et al. 2004; Ngah and Fatinathan 2008; Zhou et al. 2009). The

1**preparation of chitosan**/rarasaponin/**bentonite** (CRB) **composite film**

and its capability for the removal of Cu (II) in aqueous solutions are reported in this paper. The incorpo- ration of three materials (rarasaponin, bentonite, and chitosan) as a composite is worthy of study because of their beneficial existence, such as they are abounded in nature, inexpensive, and possible to be applied to industrial scale. The unique feature of the prepared composite due to molecular interac- tions of the three materials are discussed. The reusability and stability of the prepared composite are also investigated. Materials and method Materials The raw materials for the preparation of composite are obtain- ed from local areas in Indonesia; chitosan (85% deacetylated) was obtained from Biotech Surindo, West Java; Ca-bentonite was obtained from Punung Village, Pacitan, East Java, Indonesia; and Sapindus rarak De Candole was obtained from Klaten, Central Java. Analytical grade chemicals 1,5- diphenylcarbazide, H_2SO_4, $CuSO_4 \cdot 5H_2O$, Na_3PO_4, CH_3COOH, NaOH, NaCl, HCl, and C_6H_6 were

20**purchased from Sigma Aldrich and used without further purification. Preparation of rarasaponin**-impregnated **bentonite**

(rarasaponin-bentonite) A total of 200 g of bentonite is activated by immersing it into 600 mL of 3 N H_2SO_4 solution for 2 h at a temperature of 373 K. The acid-activated bentonite (AAB) is cooled to room temperature and then continued with sonication for 1 h. AAB is rinsed continuously using deionized

2**water until the pH of the rinse water**

reaches 6. AAB is then subjected to microwave irradiation with a strength of 700 W for 10 min. Next, the AAB is dried using a 378 K oven for overnight. Sapindus rarak DC fruits are washed to remove dirt. The fruits are then dried at 353 K and pulverized into

2**a particle size of + 180/− 200 mesh. Rarasaponin**

is obtained from the fruits by extracting dried-fruit powder with methanol in a mass-to- volume ratio of 1:3.75. Extraction

27**was heated at** 323 K **for 60 min** with a constant **stirring** 200 **rpm**

. Subsequently, the supernatant

5was separated from the solid by centrifugation at 4900 rpm for 4 min. The methanol was removed from the supernatant by

using rotary vacuum evaporator. The obtained rarasaponin crystal was collected from the evaporator flask and kept in an airtight container. Rarasaponin-bentonite was prepared using a simple im- pregnation method. Briefly, 1 g of rarasaponin was dis- solved

26in 100 mL deionized water. The solution was heated to 353 K for

30 min with a constant stirring 300 rpm. Subsequently, 10

10g of AAB was added to the rarasaponin solution, and the mixture is stirred for

another 30 min. The mixture was then irradiated in a

27microwave at a heating power of 700 W for

1 min. The rarasaponin-bentonite was dried at 378 K for 36 h, and then, the particle size was reduced to 100/200 mesh. Preparation chitosan/rarasaponin/bentonite composite f ilm The chitosan/

2rarasaponin/bentonite (CRB) composite film was prepared according to the following procedure

: 1 g of chitosan was dissolved in a 100 mL of 1 M acetic acid solution at 353 K for 1 h. Subsequently, 3

3g of rarasaponin–bentonite was added to the chitosan solution. The mixture was heated

at 353 K for 3 h with a

1constant stirring 500 rpm. The obtained CRB solution was

then poured into the molding-tray with a liquid height of 1 mm and then dried at 333 K for 48 h. Dry CRB was placed in an airtight container until subsequent use. Characterization of the adsorbents The functional group of the adsorbent was characterized by using Fourier transform infrared (FTIR) spectroscopy (Shimadzu FTIR 8400S) at a wavenumber range of 4000– 500 cm^{-1}. The X-ray diffraction (XRD)

2analysis was per- formed by using a Philips X’pert Xray diffractometer with a Cu Kα1 radiation at λ = 0.1541 nm. Nitrogen sorption iso- therms were conducted by using a Micromeritics ASAP 2010

23at a temperature of − 176 °C and a relative pressure range of 0.005 to 0

.995. The

17point of zero charges (pHpzc) was determined by using the pH-drift method; the detailed

procedure can be found elsewhere (Laysandra et al. 2019). qe ¼ ðCo−CeÞ m ?V ð2Þ where Co

8is the initial concentration of heavy metal in the solution, mg/L; Ce is the equilibrium concentration of heavy metal, mg/L; V is the volume of the solution, L; and m is the mass of the adsorbent, g

. As

5for the adsorption kinetics, three different Cu(II

) initial concentrations (100, 300, and 500 mg/ L) and 0.3 g adsorbent was used. The sampling was done

18at a certain time interval. The concentration of Cu(II) ions was determined by

using the 1,5-diphenylcarbazide method. The concentration was determined by measuring the absorbance at 540 nm using a UV-Vis spectrophotometer (UV-1700 PharmaSpec, Shimadzu). The detailed procedure can be found elsewhere (Turkington and Tracy 1958). Reusability test Reusability of the prepared composite was tested by conducting six adsorption-desorption cycles

7at a temperature of 303 K. Adsorption was

conducted by using 0.3 g adsorbent and initial Cu(II) concentration of 500 mg/L for 4 h. Desorption was carried out in 0.5 mol/L HCl solution as the eluent; the Cu(II) loaded-adsorbent is gently shaken in eluent for 4 h, then the intact adsorbent was taken and used for another consecutive cycle. Adsorption experiments

13The effect of temperature and pH in the removal of Cu(II) was studied. The

temperature range studied is 303 to 343 K, while the pH range studied is 2 to 7, at a constant temperature of 303 K. The pH of the solution was adjusted by using 0.1 N sodium hydroxide or hydrochloric acid solution. An initial Cu(II) concentration of

12500 mg/L and adsorbent mass of 0.3 g was used, and the

2adsorption was conducted for 4 h in a thermostated shaker water bath

. Removal efficiency is expressed as a percentage value calculated using the following equation: %Removal ¼ Co−Ce ? 100% ð1Þ Co

6The adsorption isotherms of Cu (II) on AAB, chitosan, and

CRB composite were obtained isothermally at 303, 323, and 343 K. A known amount of adsorbents (0.1–1.0 g) was added into iodine flasks (each contains

3100 mL of Cu (II) solution with the concentration of 500 mg/L). The flasks were

placed into the shaker water bath and shaken

29at 200 rpm for 4 h. The solid was separated from the solution by centrifugation at 5000 rpm for 10 min. The amount of

Cu(II) adsorbed at equi- librium condition (qe) was determined according to the eq. (2). Result and discussion Characterization of the adsorbents Surface functional groups of the adsorbents analyzed using FTIR are presented in Table S1. The characteristic peaks of each composite raw materials were observed to confirm their in- volvement in the composite structure (Table 1). The main char- acteristic peaks of rarasaponin which have been identified for the

1C=O stretch of the carbonyl ester group

, C–H bend at hy- droxyl group,

1C–O stretch of deacylated carbonyl group

, and C=C stretch of aromatic rings, are observed at wavenumbers 1699.17, 1361.65, 1286.43, and 1056.92 cm−1, respectively. The main peaks of chitosan which correspond to C=O in amide group, –NH2 in the amino group, –NH bend, O–H vibration, and C–H vibration are observed at 1768.60, 1596.95, 1506.3, 1423.37, and 1325.01 cm−1, respectively. The main peaks of AAB associated with the silanol and alumina group were ob- served at wavenumbers 1051.13, 935.41, 671.18, 478.31, and 453.24 cm−1; where they refer to

9Si–O–Si stretch in tetrahedral layer, Al–Al–OH bend, Si–O

stretch on silica and

10quartz, Si–O– Al bend in octahedral Al, and Si–O–Si bend, respectively

. Enhanced characteristic peaks derived from the raw materials (rarasaponin, chitosan, and AAB) were observed in CRB Table 1 The FTIR analysis of raw matrials, rarasaponin, chitosan, and CRB composite Functional Group Rarasaponin Chitosan AAB CRB composite O–H stretch (alcohols or phenols)

9O–H stretch of silanol (Si–OH) groups C=O

in amide group C=O stretch (Ester carbonyl group) O–H bend, for adsorbed H_2O at bentonite interlayer NH_2 in amino group NH bending vibration in amide group

1O–H vibration in amide ring

3C–H bend bonded with hydroxyl group C

–H vibration in amide ring

1C–O stretch of deacylated carbonyl group

3C=C stretch (aromatic rings group

)

9Si–O–Si stretch of the tetrahedral layer Al–Al–OH bend Si–O

stretching of silica and

10quartz Si–O–Al bend (for octahedral Al) Si–O–Si

bend - - - - - 1768.6 1699.17 - - - - 1596.95 - 1506.30 - 1423.37 1361.65 - - 1325.01 1286.43 - 1056.92 - - - - - - - - - - - 3847.72 2929.67 - - 1647.10 - - - - - - - 1051.13 935.41 671.18 478.31 453.24 3865.08 2935.46 1656.74 1629.74 - 1539.09 1413.72 - 1382.87 - 1286.43 - 1029.92 - 659.61 503.39 472.53 composite, suggesting that raw materials were successfully em- bedded in the CRB composite. Some of the enhanced charac- teristic peaks are as follows: the presence of carbonyl groups from rarasaponin is indicated by the wavenumbers 1699.17 and 1286.43 cm^{-1}; amide groups from chitosan are indicated by the wavenumbers 1656.74 and 1413.72 cm^{-1}; and silanol groups from AAB indicated by the wavenumbers 2935.46, 1029.92, 659.61, 503.39, and 472.53 cm^{-1}. The crystallinity of AAB and CRB composite is character- ized by XRD analysis; the diffractograms are presented in sup- plementary data Fig. S1. The diffraction peaks contributed to the crystal planes of montmorillonite is observed for both AAB and CRB; specifically, at 2θ = 6.1, 22.1, 30.1, and 35.9° for AAB, at 2θ = 5.8, 19.8, 31.3, and 36.2 for CRB composite. The reduced intensity of 001 planes for CRB compared to AAB suggests the intercalation of rarasaponin; moreover, the typical 001 diffrac- tion plane shows an alteration from 6.1° (in AAB) to 5.8° (in CRB). The basal spacing measurement for AAB at 2θ = 6.1° is 1.45 nm, and for CRB at 2θ = 5.8° is 1.52 nm. The increase in basal is due to the intercalation of rarasaponin in the interlayer of montmorillonite. The characteristic peaks in other 2θ belong to a crystal plane of quartz, kaolinite, and illite. Nitrogen sorption isotherms of

1**AAB and** CRB **are provided in supplementary data** Fig. **S2**

. A combination of sorption isotherm plot type I and IV was observed for AAB, Fig. S2(a). The type I isotherm behavior indicated by a steep pore filling with volume adsorbed of 25 cm3/g

2**at a low relative pressure (P**/P0), **this** charac- teristic **indicates** the presence **of**

microporous structure. Transition to the type IV isotherm at higher P/P0 with larger pore filling indi- cate the presence mesoporous structure in AAB. The presence of micro-mesoporous in AAB is supported by the DFT pore size distribution (5–150 A or 0.5–15 nm), as shown in the inset in Fig. S2(a). The nitrogen sorption isotherm for CRB also show a combi- nation of isotherm plot type I and IV but with the steeper pore filling at high P/P0. The steeper pore filling suggests a more complex structure of the adsorbent, which is most likely due to the incorporation of rarasaponin and chitosan into AAB creating a multilayered structure. Furthermore, a nearly vertical plot at P/P0 close to 0.99 indicates delayed desorption due

15**to the** multilayer **structure of** CRB (Lu **et al**. 2017; Sotomayor **et al**

. 2018). The

23**formation mechanism of** the CRB **composite** CRB **composite was prepared**

by combining the rarasaponin- impregnated bentonite with chitosan in an acidic solution. The formation mechanism of the CRB composite is graphically pre- sented in Fig. 1; the two main mechanisms are the impregnation of bentonite by rarasaponin and particle incorporation by chitosan. The impregnation of bentonite-rarasaponin occurs due to a charge difference between the two particles. Bentonite used in impreg- nation has been acid-activated; the activation process causes the silanol group, Si–OH, to be protonated to Si–OH2+. As for rarasaponin, the dissolution of compound initiates disengagement of two acyl groups (–C2H3O+) and leaving two negatively charged oxygen atoms. Negatively charged rarasaponin attacks positively charged bentonite so that the impregnation process occurs (Kurniawan et al. 2011). The acidic chitosan solution was added before the formation of the CRB composite. The acidic environment causes the protonation of the amine groups in chito- san; this protonated amine then forms a bond with the deacylated rarasaponin. Molecular interaction also occurs between chitosan and bentonite, where the van der Waals hydrogen bond is the most likely interactions. The interaction between the three molecules (chitosan, rarasaponin, bentonite) leads to the formation of chito- san/rarasaponin/bentonite (CRB) composite. Adsorption studies Influence of temperature The adsorption capability of AAB, chitosan, and CRB com- posite at various temperature is given in Fig. 2. It is obvious Fig. 1 The formation mechanism of CRB composite film (octahedral sheets are not shown in silicate structures) that the CRB composite exhibits better adsorption capability compared to the parent materials. CRB has the highest remov- al efficiency of 88.59% at 303 K; removal efficiency de- creases as temperature increases. The opposite phenomenon is observed for AAB and chitosan; increase in temperature causes a

1**decrease in removal efficiency. The highest removal efficiency**

for AAB and chitosan is 28.83 and 68.70%, respec- tively, at 343 K. The temperature has two main effects in the adsorption process: (1)

7**an increase in temperature** enhances **the rate of** diffusion of **copper** ions to **the**

adsorbent; (2) if chemisorption is the control mechanism, the increase in temperature will enhance the uptake of Cu(II). In this study, the increase of 100 80 AAB Chitosan CRB % Removal 60 40 20 0 303 323 343 Fig. 2 Adsorption capability of raw materials and CRB composite at various temperatures temperature has a negative impact

33**on the removal of Cu (II) by**

CRB. This is

22**due to the attractive** force **between** Cu(II) ions, **and the surface of the adsorbent** weakens **at**

high tem- peratures so that Cu(II) ions can escape easily. Furthermore, the kinetic energy of Cu(II) ions increases at higher tempera- ture thereby increasing the

22**tendency of ions to escape from the adsorbent**

(Aksu and Kutsal 1991; Horsfall and Spiff 2005).

12**The removal efficiency of Cu(II) by** CRB decreases as **the**

temperature is raised indicating that the removal process is exothermic.

20**Influence of initial pH** Acidity or alkalinity **of the solution** controls **the**

interaction between adsorbent and adsorbate in an adsorption process. As shown in Fig. 3, the adsorption of Cu(II) in the pH range 2 to 7 was studied

28**to examine the** effect **of** alkalinity in **the adsorption process**

. It is noted that at acidic pH below 5, ad- sorption of Cu(II) by AAB and CRB is poor. The highest adsorption of Cu(II) occurs at pH 6 for AAB and pH 5 for CRB, where the maximum adsorption is 23.05 and 62.50 mg/ g for AAB and CRB, respectively. Adsorption of Cu(II) by AAB and CRB decreases as the pH is increased further. The adsorption characteristic under different alkalinity conditions can be explained by examining the electrical potential differ- ence between the adsorbate and adsorbent molecules. The electrical potential of the adsorbent can be properly described from point zero charges (pHpzc) (Komulski and Saneluta 2004). The net positive charge on the surface of 70 12 (62.50) 60 10 8 50 pHfinal 6 4 (43.33) (42.35) qe (mg/g) 40 2 (37.11) 0 0 2 4 6 8 10 12 30 pHinitial (23.05) 20 AAB (14.24) CRB (13.27) (9.49) 10 (2.27) (2.07) 0 0 2 4 6 8 pH Fig. 3 The

5**influence of pH on** the **adsorption of Cu(II) onto** AAB and CRB **adsorbent**

is achieved as the pH < pHpzc, isoelectric point is achieved as pH = pHpzc, and net negative charged is achieved as the pH > pHpzc. As shown in the inset of Fig. 5, pHpzc of AAB is 6.01 and for CRB is 4.54. This means that at pH below 5, the surface charge of AAB and CRB is positive due to the attack of H+ contained in the acidic solution; H+ ions and Cu(II) ions then compete for the active site of the adsorbent which caused drawback of adsorption of

24**Cu(II**). At **the** best **Cu(II) adsorption** pH, when pH **of the**

solution ex- ceeds pHpzc, the

33**number of active** sites **available for** binding **of heavy metal ions**

increases because H+ in the solution de- creases which leads

31**to an increase in adsorption of Cu(II**

) (Yu et al. 2016). Moreover,

17**at pH** above **pHpzc, the surface charge of the** adsorbent **is negative**

while Cu(II) ion tends to be pre- sented in the form of its divalent ion accompanied by several hydroxides species such as CuOH+, CuCO3, CuHCO3+, and Cu(OH)2. Electrostatic difference between adsorbent and Cu(II) promotes the

32**adsorption of Cu(II). A decrease in**

ad- sorption at a greater pH (> 5 for CRB and > 6 for AAB) is caused by the presence of excess hydroxide ions which cause both the adsorbent and adsorbate molecules to be negatively charged. Cu(II) ions tend to exist as Cu(OH)3− and Cu(OH)42− in solutions with an excessive amount of hydroxide ions (Khan and Wahab 2007). The repulsive force becomes dom- inant because both molecules possess the same electrostatic charge (Lu et al. 2017). Adsorption isotherm

6**The adsorption isotherms of Cu(II) on** AAB **and** CRB **are** depicted **in Fig**. 4. **The**

experimental adsorption equilibria

3were correlated using two well-known isotherm equations namely Langmuir and Freundlich. The Langmuir equation

is developed according to the following simple assump- tions: monolayer adsorption, identic adsorption sites, lo- calized adsorption, and constant adsorption energy (Langmuir 1918). The mathematic expression of the Langmuir can

13be written as ? ? q e ¼ q KLCe m 1

þ KLCe ð3Þ The parameter qm in Eq. (3) represents the maximum amount of adsorbate adsorbed by the adsorbent (mg/g). The affinity of the adsorbate towards the surface of adsorbent is represented by the KL parameter (L/mg). The Freundlich equation represents the adsorption of gases or liquids on the heterogeneous surface of adsorbents. This equation can be used to analyze the heterogeneity of the ad- sorbent surface and the energy of its active sites (Freundlich 1906).

3Freundlich equation has the following mathematical form: qe K F Ce n F ¼ 1 = ð4Þ where

KF ((mg/g).(L/mg)–n) and nF are the Freundlich adsorp- tion capacity and heterogeneity constant for the adsorption system, respectively. The fitting of experimental and calculated data was con- ducted using the non-linear least square method; the results are graphically presented in Fig. 4 while the calculated param- eters

26are given in Table 2. Based on the values of R2, the

data fitting using Langmuir equation is better than Freundlich, in- dicating that the adsorption of Cu(II) on CRB and AAB oc- curs at the homogeneous sites of the adsorbent (Lu et al. 2017). The isotherm adsorption was done at three different temperatures of 303, 323, and 343. The maximum adsorption capacity of Cu (II) by CRB composite at 303, 323, and 343 K are 412.70, 386.47, and 359.60 mg/g, respectively. It is also proven from the isotherm data fitting that adsorption by CRB occurs exothermically. The data fitting using the Freundlich equation supported exothermic adsorption process by CRB, in which the KF value decreased with the increase of tempera- ture. Comparison of CRB adsorption capacity against other adsorbents on Cu(II) is shown in Table S2. CRB exhibits an outstanding adsorption capacity compared to the other similar adsorbents indicates that CRB can be a potential adsorbent for

24Cu(II). Adsorption kinetics The pseudo-first (Corbett 1972) and pseudo- second-order

(Ho and McKay 1999) equations

14were employed to correlate the kinetic experimental data. The pseudo-first and pseudo- second-order equations are expressed as eq. (5) and

(6), re- spectively: qt ¼ qe1ð1−expð−k1tÞÞ ð5Þ Fig. 4

6**Adsorption isotherms of Cu(II) on** a AAB **and b**

CRB 30

1**30°C 45°C 60°C Langmuir** model **Freundlich** model (a) **qe**

(mg/g) 20 10 0 0 100 200 300 400 500

34**Ce (mg/L**) 250 (**b**) 200 **qe (mg/g**) 150 **100**

50 0 0 100 200 300 Ce (mg/L) Table 2 The parameters of Langmuir and Freundlich equations for the adsorption of Cu(II) on AAB and CRB Adsorbent and temperature

30**Langmuir Freundlich qm (mg/g) KL (L/mg) R 2 KF (mg/g**)(mg/**L)−n**) nF **R 2**

AAB 303 K 57.40 0.0017 0.9968 0.5967 1.6415 0.9962 323 K 59.57 0.0018 0.9984 0.7233 1.6822 0.9978 343 K 64.70 0.0019 0.9969 0.8151 1.6954 0.9958 CRB 303 K 412.70 0.0047 0.9958 5.9704 1.5202 0.9799 323 K 386.47 0.0038 0.9785 4.6719 1.4942 0.9551 343 K 359.60 0.0035 0.9964 4.1063 1.4887 0.9841 qt ¼ qe2 1 qþe2qke22tk2 ? ? ð6Þ where

15**qt (mg/g**) shows **the** uptake **of heavy metal adsorbed** by the adsorbent **at**

a certain

16**time, t (min**). Parameters **k1** (1/**min) and k2 (g/mg.min) are the** time constant for **the pseudo-first and pseudo-second-order models, respectively**. Parameters qe1 **and** qe2 are **the**

amounts of Cu (II) adsorbed at equilibrium condition.

12**The effect of initial Cu(II) concentration** on the adsorption **was** also investigated **in the**

kinetic study, where the initial Cu(II) concentration studies are 150, 300, and 500 ppm. The fitting on the adsorption kinetics data

2**using the pseudo-first and pseudo-second-order** equations **are** given **in Fig**. 5; **the parameters** of both equations **are** presented **in Table** 3. **The**

R2 value for

2pseudo-second-order fitting is closer to 1 compared to that

1pseudo-first-order fitting, in- dicates that the pseudo-second-order equation represents the kinetic data better. Better fitting to the pseudo- second-order

equation shows that the interaction between the adsorbate and the adsorbent is chemisorption con- trolled. The fact that the adsorption capacity decreases as the temperature increases indicates that the chemisorption is exothermic in this study (Arshadi et al. 2014). The effect of initial Cu(II) ion concentrations to the adsorption is also illustrated in Fig. 5. The increase in Cu(II) adsorption ca- pacity

6with increasing Cu(II) initial concentrations indi- cates that the

concentration gradient plays an important

25Fig. 5 Adsorption kinetics of Cu(II) on a AAB and b

CRB 25 (a) 20 qt (mg/g) 15 10 100 ppm 300 ppm 5 500 ppm Pseudo First Order Pseudo Second Order 0 0 50 100 150 200 250 t (min) 100 (b)

3480 qt (mg/g) 60 40 20 0

0 50 100 150 200 250 t (min) Table 3 The

11parameters of the pseudo-first and pseudo-second-order models for the adsorption of Cu (II) on AAB and

CRB (T = 30 °C and

1mass adsorbent = 0.5 g) The initial concentration of Cu (II) (ppm) Experimental result Pseudo-first order Pseudo-second order qeexp (mg/g) k1 (min−1) qe1 (mg/g

) R2 k2 (mg g−1 min−1) qe2 (mg/g) R2 AAB 100 10.6993 0.1832 10.3986 0.9863 0.0293 10.8463 0.9998 300 16.8234 0.1853 16.2349 0.9738 0.0184 16.9666 0.9975 500 23.2965 0.1880 22.0302 0.9592 0.0128 23.1194 0.9926 CRB 100 19.2690 0.1866 19.0343 0.9816 0.0171 19.8003 0.9953 300 54.5788 0.3003 54.0150 0.9905 0.0118 55.3369 0.9980 500 84.7710 0.3493 83.6714 0.9921 0.0098 85.3768 0.9990

18role in the adsorption process. Cu(II

) ions in solution pro- ΔS° ΔH ° vide

18**a driving force** that supports **mass transfer between**

In K ¼ R − RT ð9Þ adsorbate and adsorbent molecules; the higher the initial concentration of Cu(II) causes the resistance to mass trans-

21**where K is the equilibrium constant** that **can be obtained** by fer **to** weaken. Moreover, **the**

weakening of resistance to plotting In (qe/Ce) vs. Ce then extrapolating to zero. The other mass transfer encourages electrostatic interactions between parameters, R is gas constant (8.314 J/ mol.K), and T is abso- metal ions and adsorbent so that the adsorption capacity lute temperature (K). increases (Kurniawan et al. 2011; Arshadi et al. 2014). The calculated thermodynamic parameters are given in Table 4. The negative ΔG° confirms the feasibility and sponta- neity of Cu(II) adsorption by CRB; however, ΔG° becomes Thermodynamic parameters more positive as temperature increases indicating that spontane- ity declines at a higher temperature. Exothermic behavior of Thermodynamic parameters, specifically enthalpy change Cu(II) adsorption on CRB is shown from the negative ΔH° (

5**ΔH°), entropy change (ΔS°), and Gibbs free energy**

value, asserting that the adsorption of Cu(II) is more suitable at change (ΔG°), are crucial parameters in determining the low temperatures. Positive ΔS° indicates randomness in the im- spontaneity and suitability of an adsorption process. The mobilization of metal ions on the active sites of the adsorbent in value of ΔG° can be calculated using the following equa- the adsorption process which allows for spontaneous adsorption. tion: In

13**the adsorption of Cu(II) by** AAB, **the process**

also runs spon- ΔG° ¼ −RT lnK ð7Þ taneously as indicated by negative ΔG°. The

32**positive value of ΔH**° indicates **endothermic adsorption of Cu(II**

) onto AAB. The In a constant pressure and temperature, the relation of ΔG°, affinity of Cu(II) towards AAB is weaker than towards CRB as ΔH°, and ΔS° can be expressed as the following equation: indicated by the higher positive ΔS° of CRB. ΔG° ¼ ΔH°−T:ΔS° ð8Þ Reusability and stability of CRB adsorbent The

7**values of ΔH° and ΔS ° are** shown by **the** slope **and intercept of the** Van’t Hoff **plot In K vs 1/T**: The reusability **of**

CRB adsorbent was investigated by performing adsorption-desorption cycles at 303 K. As

28**Table 4** The **thermodynamic parameters for the adsorption of** Temperature AAB copper (**II) ions**

on AAB and CRB (K) ΔG° kJ/ mol CRB

11**ΔH° kJ/ ΔS° ΔG° kJ/ ΔH° kJ/ ΔS° mol J/mol**·K **mol mol** J/**mol**

·K 303 323 − 6.15 − 6.58 3.5 5.13 − 1.37 − 0.63 − 2.45 87.2 343 − 6.90 − 0.41 Fig. 6 Reusability and degradation test of CRB composite shown in Fig. 6, the CRB composite was still capable of removing 75.5% Cu(II) after 6 consecutive cycles. However, the decrease in CRB mass caused by particle detachment was also observed in each cycle. After six cy- cles, 82.5% of the adsorbent mass remains; some parts of the CRB adsorbent are detached from the starting material which is due to the chitosan degradation. It is evident that CRB composite can be reused and regenerated even though

25**there is a decrease in the removal** efficiency **of** Cu (**II**

) at each regeneration stage accompanied by the break- down of CRB particles. Apart from the breakdown of CRB composite, it has several advantages, that is high adsorp- tion ability compared to some reported adsorbents (Table S2), inexpensive raw materials, and environmental- ly friendly properties. Conclusion A new composite material with high adsorption capacity to- wards Cu(II) was successfully prepared by combining chito- san–rarasaponin–bentonite (CRB) through a straightforward impregnation and irradiation process. The

5**adsorption of Cu(II) onto** CRB composite **is** an **exothermic**

21**process, the maximum adsorption capacity** of CRB is **found to be** 412.70 **mg/g**

at 303 K. The isotherm and kinetics adsorptions are well represented by Langmuir and pseudo-second-order model. The negative values of ΔG° confirm the feasibility and the spontaneity of Cu (II) adsorption by CRB.

15**In addition to** its **high adsorption capacity**

, CRB can be reused and regen- erated. CRB still able to remove up to 82.5% of Cu(II) after 6 adsorption-desorption cycles.

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