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1**Aqueous sorption of tetracycline using rarasaponin-modified nanocrystalline cellulose** Vania **Bundjaja** a, Tirta Mutiara **Sari** a, Felycia Edi **Soetaredjo** a,b, Maria **Yuliana** a, **Artik Elisa** Angkawijaya c, **Suryadi**

Ismadji a,b, Kuan-Chen Cheng d,e,f, Shella Permatasari Santoso a,b,∗ a

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article info Article history: Received 7 October 2019 Received in revised form 27 December 2019 Accepted 31 December 2019 Available online xxxx Keywords: Cellulose Nanocrystal Rarasaponin Surface modification Tetracycline Drug delivery abstract

1**The sorption ability of NCC and its modified form against tetracycline were investigated. NCC modification was carried out using a natural surfactant, namely rarasaponin, to improve the NCC adsorption capacity. The** modifi- cation **was made with a mass ratio of NCC to rarasaponin 10:1 (10N1R) and 20:1 (20N1R). The modified NCC characteristics were investigated using Fourier transform** infrared (**FTIR), zeta potential analyzer, X-ray** diffrac- tion (**XRD), and scanning electron microscope (SEM). There are no structural changes to the surfactant- modified NCC, as revealed by SEM. However, other characterizations show that the incorporation of rarasaponin indeed altered some characteristics of NCC. The modified NCC shows higher adsorption capacity towards TET. The adsorption capacity of TET was 13.97, 16.47, and 18.11 mg/g (at 60 °C) for NCC, 10N1R, and 20N1R**, respec- tively. **The kinetic release (desorption) study of** TET@20N1R **showed a release efficiency of 18.28% at pH 3 and 55.49% at pH 7**

 1. Introduction The use of nanoparticles for applications in the medical field, such as drug carriers, has been widely anticipated. Many studies have shown that modification of particle size to nano can improve material compat- ibility. In addition, nanoparticles have superior characteristics such as high surface to mass ratio, good adsorption ability, modifiable selectiv- ity, and easy degradation. Over the years, various synthetic polymers such as poly(lactic-co-glycolic acid) (PLGA), poly(ε-caprolactone), poly(ethylene glycol) (PEG), and poly(N-(2-hydroxypropyl) methacrylamide) (PLG), has been widely used to prepare nano-sized drug carriers [1]. The use of synthetic polymers has several limitations, especially in their high immunogenicity, which causes adverse effects on their long-term use [2,3]. For this reason, the use of natural polymers such as chitosan, alginate, collagen, and cellulose, for the synthesis of drug carriers has received much attention [4]. ∗ Corresponding author at:

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(S.P. Santoso).

2**Nanocrystalline cellulose (NCC) is** a **nano-sized**

particle derived from a natural polymer, cellulose, whose modification has been extensively studied. The vast interest in NCC is due to its high biocompatibility, which is assisted by other superior properties, such as abundantly avail- able, natural, and non-toxic. Structurally, the surface of NCC is rich in hy- droxyl groups, which provide modification sites for many functional applications. Surface modification of NCC is a common practice of cellu- lose modification for the preparation of drug-carriers and other ad- vanced materials [5–11]. Some surface modification techniques available are esterification, cationization, sulfonation, oxidation, silylation, esterification, functional compound or polymer grafting, and carboxylation. Surface modification of NCC by incorporating functional compound is widely performed among the available techniques. This is because other modification techniques (e.g., oxidation) often alter the structure of the NCC, which can result in decreased surface area, structural stability, and mechanical strength [8–10]. In this study, we investigated the effects of a natural surfactant (i.e., rarasaponin, as a surface modifying agent) on the ability of NCC as a drug loading and releasing the device. Rarasaponin is extracted from Sapindus rarak DC; so far, it has been used as a modifying agent https://doi.org/10.1016/j.molliq.2019.112433 0167-7322/ for clay materials to remove various hazardous substances from water or wastewater. The results show that the incorporation of rarasaponin into clay can significantly increase the adsorption capacity of clay [12–14]. Here, rarasaponin is incorporated with NCC before im- proving the drug adsorption capacity, which yet to be done to date. Modification of NCC with surfactants (other than rarasaponin) has been carried out [7,15,16]. For instance, Jackson and co-researchers used cetyltrimethylammonium bromide (CTAB) to modify NCC; they reported that only ~6% (from 100 μg) paclitaxel drug could be loaded onto 2 mg of unmodified NCC, while up to ~85% paclitaxel could be loaded onto 2 mg of NCC modified with 12.9 mM CTAB [7]. Natural sur- factant (i.e., rarasaponin) was chosen since natural surfactants are envi- ronmentally friendly materials that are generally more easily degraded, less toxic, and also easily digested; compared to synthetic surfactants [17]. Tetracycline is a widely used antibiotic that works against gram- positive and gram-negative bacteria. It has three ionizable functional groups that can undergo protonation/deprotonation depending on the pH of the solution (Fig. S1) [18,19]. The main challenge for tetracycline administration is to increase drug bioavailability [20]. Antibiotic drug delivery system is essential for eradicating microorganisms associated with bacterial infections and causing lower doses, toxicity reduction, extended-release, and minimizing systemic exposure [21]. The loading capacity of rarasaponin-modified NCC was investigated by means of ad- sorption studies on tetracycline drugs. Drug desorption kinetics were also performed and modeled. 2. Materials and methods 2.1. Materials Analytical grade sulfuric acid (H_2SO_4, 95–98% purity), sodium hy- droxide (NaOH, ≥97% purity), disodium hydrogen phosphate (Na_2HPO_4, ≥99% purity), potassium dihydrogen phosphate (KH_2PO_4, ≥99% purity), phosphoric acid (H_3PO_4, 85 wt% in H_2O), sodium chloride (NaCl, ≥99% purity), and tetracycline ($C_{22}H_{24}N_2O_8$, ≥98% purity) were purchased from Sigma-Aldrich (Singapore). Sapindus rarak DC fruits were obtained from Malang, East Java, Indonesia. Reversed osmosis (RO) water was used in this study to dissolve chemicals and treat sam- ples. Dialysis membrane tubes (MWCO 12–14 kD) were purchased from Spectrum Laboratories, Inc. 2.2. Preparation of cellulose nanocrystals NCC

3**was prepared from filter paper (Whatman #1**) through **the**

hy- drolysis process using concentrated sulfuric acid [9,22]. Briefly, 10 g fil- ter paper was soaked in 87.5 mL of H_2SO_4 solution (64 wt%). The hydrolysis was carried out for 1 h at 45 °C with constant stirring. Sub- stantial amounts of cold water were then added to stop hydrolysis; two layers (suspension layer and clear layer) were then formed. The cloudy suspension layer was collected and then centrifuged at 10,000 rpm for 10 min. The centrifuged solids were then put into a dial- ysis tube against RO water; the water was continuously changed until the pH of the dialysate reached 6. The neutralized suspension was then ultra- sonicated for 30 min and kept at −40 °C before freeze- drying. 2.3. Rarasaponin extraction Rarasaponin was extracted from the Sapindus rarak DC fruits accord- ing to a previously reported method [13]. Briefly, dried- fruit seeds were removed from pericarps. Subsequently, the pericarps were pulverized to obtain powdered fruit. 50 g of fruit powder extracted with 500 mL of distilled water,

9at 80 °C for 1 h with constant stirring. The rarasaponin extract was separated from the

1solid residue using centrifugation at 4000 rpm for 10 min. The rarasaponin dry extract was

obtained by oven drying at 80 °C, followed by air drying for 24 h. The extracted rarasaponin was quantified for its saponin content using a sulfuric- vanillin reagent according to the method reported by Hiai and groups [23]. The total saponin content of the extracted rarasaponin was 18.82 ± 0.19% from dry fruit weight. 2.4. Surface modification of NCC The surface modification of NCC was carried out under different NCC-to-rarasaponin mass ratios (10:1 and 20:1). For simplicity pur- poses, samples were denoted as 10N1R and 20N1R for a sample of the NCC-to-rarasaponin ratio of 10 and 20, respectively. 10N1R was pre- pared by slowly adding

21 g NCC suspension (in 100 mL RO water) to

0.1 g rarasaponin in 100 mL RO water.

7The mixture was heated at 45 °C for 1 h under constant stirring. The unbound rarasaponin was sep- arated using a

centrifuge that operates

20at 10,000 rpm for 10 min. The resulting NCC

-rarasaponin (NCC/Rara) was dried in a freeze dryer. The same procedure was used to prepare 20N1R, except the rarasaponin so- lution, was prepared by dissolving 0.05 g of rarasaponin in 100 mL of RO water. 2.5. Characterization The surface functional groups were determined using Fourier Trans- form Infrared (FTIR) analysis using a

4Shimadzu 8400S; the KBr pellet was used as the background, and the measurements were conducted at wavenumber range of 4000–400 cm−1

. Zeta Potential analyzer (Brookhaven 90Plus) was employed to measure the surface charge of the samples (0.01%wt in deionized water) at various pHs. X-ray diffrac- tion (XRD) patterns were recorded at 40 kV and 30 mA using a Rigaku Miniflex Goniometer with Cu Kα radiation, while the surface topogra- phy was acquired using surface electron microscopy analysis on a JEOL JSM-6500F with Pt coating and 5.0 kV acceleration voltage. A Java- based image processing and analysis program, namely ImageJ, was

20used to determine the dimension of the NCC

and NCC/Rara crystal particles. 2.6. Adsorption study Tetracycline (TET) adsorption was studied isothermally at vari- ous temperatures (30, 45, and 60 °C). The TET adsorbate was pre- pared at a concentration of 100 ppm in phosphate buffer at pH 3. The choice of pH was based on the previous study by Wijaya et al. which shows that the adsorption capacity at pH 3 was the highest; this is since TET present as cations at pH b 3.3 [24]. Various NCC masses (10–20 mg) were then introduced in closed-dark-flasks con- taining 10 mL of prepared TET solution. The flasks were put in a ther- mostatic

> 7**shaking water bath (Memmert** type **WB-14**) and operated **at** 200 **rpm for** 8 **h**

. Subsequently, the suspension was separated by centrifugation. The unadsorbed (unloaded) TET

> 1**was measured using a spectrophotometer at** an optical density **of** 610 **nm** (OD610). **The**

amount of TET adsorbed (loaded) on NCC was calculated accord- ing to Eq. (1): qe ¼ C0−Ce

> 7**m V** ð1Þ **where qe is the amount of** TET **adsorbed** per **g**

of adsorbent,

> 5**C0, and Ce (mg/L) are the initial and** residual concentration **of** TET, **respectively. V (L) is the total volume of the investigated system, and m (g) is the mass of**

NCC added. The kinetic adsorption of TET onto NCC or NCC/Rara was studied

> 5**at a pH of** 3 **and** a **temperature of 30 °C**

. 20 mg of adsorbent was suspended in 10 mL of 100 ppm TET solution and then

> 2**shaken in a** thermostatic shaking **water bath at** 200 rpm. **The** concentration **of**

residual TET was measured at a certain interval of time. The

> 2**amount of** TET **adsorbed at** a **certain time interval was calculated by using Eq**

. (2): qt ¼ C0−Ct m V ð2Þ where qt (

> 2**mg/g) is the** uptake **of** TET **at time t**, and Ct (**mg/L) is the concentration of** TET **at time t**

. 2.7. Release kinetic study The in vitro drug release experiments were performed at 37 °C in a phosphate-buffered solution. The study was conducted at pH 3 and 7 to mimic the pH of gastric acid in the human stomach lumen and body fluid, respectively. A release study was conducted on a drug carrier (sample) that provided the highest amount of TET loaded. Drug release was carried out by suspending 20 mg of freeze-dried TET-loaded NCC/ Rara (TET@NCC/Rara) in 10 mL of phosphate buffer. The suspensions were

14**placed in a** thermostatic shaker **water bath and shaken at** 200 **rpm. At**

a specific interval time, the tube was taken and centrifuged. The concentration of released drug was determined by using a spectro- photometer at OD610. 3. Result and discussion 3.1. Preparation of NCC-rarasaponin (NCC/Rara) 3.1.1. The formation mechanism of NCC/Rara Nano-sized cellulose crystals (NCC) were obtained from the hydro- lysis of cellulose using sulfuric acid. The formed NCC crystals contain abundant hydroxyl (OH) groups and approximately 1 sulfate ester group in each 6 OH groups [9,25]. The OH group in the sixth position is the primary alcohol in which the modifications occur [26]. The incor-poration of rarasaponin then occurs via hydrogen bonds [27]. The inter- molecular hydrogen bonds involve the oxygen atom at the carboxyl group of rarasaponin (partial negative charge) and hydrogen atom at OH group of NCC (partial positive charge). The overall formation mech- anism of NCC/Rara is depicted in Fig. 1. 3.1.2. Characterization of NCC/Rara The NCC/Rara was prepared at two different NCC-to-rarasaponin mass ratio, that is 10N1R and 20N1R. Several characterizations such as FTIR, Zeta potential, XRD, and SEM were conducted to characterize sam- ples (rarasaponin, NCC, 10N1R, and 20N1R). Surface functional groups of rarasaponin, NCC, and NCC/Rara were determined using FTIR analysis, and the results are presented in the Supplementary data Fig. S2 and Table S1. A broad absorption peak was observed at 3310–3269 cm−1, which refers to OH stretching; this was observed in all samples. Meanwhile, the bending vibration of OH due to the relationship of water molecules was observed at 1632–1611 cm−1. A peak at 1254–1244 cm−1, indicating the presence of sulfonate groups, was noted for NCC and NCC/Rara. The addition of rarasaponin induces changes in several NCC absorption peaks. For in- stance, the absorption peak which corresponds to OH stretching was ap- peared at a lower frequency in NCC/Rara (3275–3171 cm−1) compared to NCC (3277 cm−1); this suggests the involvement of the OH group in the formation of NCC/Rara. The shifting to the lower frequency is due to the disappearance of some of OH groups [28] as they bounded with rarasaponin. The peak corresponding to C_C stretching appeared only in rarasaponin (1685 cm−1), and NCC/Rara (1694–1695 cm−1), indi- cates the presence of rarasaponin in NCC/Rara. The zeta potential values of the NCC and NCC/Rara were shown in Fig. S3. In the pH range of 2 to 10, a negative surface charge of NCC with a net surface charge of −6 to −8 mV was observed. Incorporation of rarasaponin causes the net surface charge of NCC to be more nega- tive; that is −8 to −11 mV for 10N1R and − 11 to −14 mV for 20N1R. The increase in surface charge negativity is caused by the pres- ence of deacylated carbonyl groups originating from rarasaponin. Putro and coworkers also observed a similar phenomenon in the de- crease of net surface charge (becoming more negative) due to the mod- ification of NCC using anionic surfactants. The zeta potential of NCC decreased from −25.24 to −37.92 mV after modification with anionic SDS [15]. The XRD patterns of NCC and NCC/Rara were given in Fig. S4. It can be seen that all samples possess major peaks at 2θ = 15°, 16.5°, and 22°, which respectively represent 101, 10ĩ, and 002 planes. The XRD pat- tern of NCC/Rara shows no significant difference compared to NCC. The

3**crystallinity index (CrI) of the samples was** calculated **from the**

pub- lished equation [29]; the detailed calculations were provided in Fig. 1. The proposed formation mechanism of NCC/Rara. Supplementary data Table S2. CrI of 74.6, 70.9, and 71.2% were obtained for NCC, 10N1R, and 20N1R, respectively. The crystallinity of NCC/Rara was found to be slightly lower than NCC. The intensity of the 002 plane for NCC/Rara was smaller than NCC itself; but, the intensity at 101 and

10ĩ planes was greater for NCC/Rara. The decrease in CrI is due to the incorporation of the non-crystalline rarasaponin [9,15,30].

9**SEM analysis was** carried out **to observe the** morphological **of**

NCC and NCC/Rara. The SEM image (Supplementary data Fig. S5) shows a rod-like crystal structure of NCC. The estimation on crystals dimensions using ImageJ shows that the synthesized NCC have a particle length of 237.4 ± 52.0 nm, and particle width of 29.9 ± 5.9 nm. Surface modifica- tion of NCC using rarasaponin does not cause any alteration in the mor- phological appearance of NCC. However, the dimension analysis shows that the incorporation of rarasaponin produced larger particle sizes. The NCC/Rara has a particle length of 356.3 ± 60.7 nm and a width of 52.3 ± 8.2 nm. 3.2. Adsorption mechanism of TET on NCC/Rara NCC/Rara contains unoccupied sulfate ester sites and deacylated car- bonyl sites, as shown in Fig. 1. These active sites play an essential role in attracting TET molecules. In Fig. 2, the illustration of TET loading onto 10N1R (higher rarasaponin concentration) and 20N1R (lower rarasaponin concentration) are shown. Attachment of cationic TET onto 10N1R or 20N1R induced by electrostatic interactions [9,15,19]; that is between the positively charged amide group of TET against sul- fate ester and the deacylated carbonyl group of NCC/Rara. Based on the phenomena observed in the adsorption study (discussed in the next section) and the concentration of rarasaponin, we proposed two different mechanisms of TET loading onto NCC/Rara: (I) At high rarasaponin concentration, TET@10N1R. In this case, the number of rarasaponin molecules is over-numbered NCC; thus, some rarasaponin molecules cannot be successfully bound to NCC particles. Furthermore, the unbounded rarasaponin molecules interact to form micelles. Later on, these micelles cause interference with the adsorption of TET onto 10N1R, thereby reducing adsorption efficiency. (II) At low rarasaponin concentration, TET@20N1R. In this case, the number of NCC particles is sufficient to accommodate rarasaponin molecules; thus, the formation of micelles is mini- mized, thereby more TET molecules can be loaded onto the adsorbent. 3.3. Adsorption isotherm study In the present study, Langmuir and Freundlich were fitted to the ex- perimental data to understand the interactions between adsorbate and adsorbents [30–32]. The Langmuir model

5**is mathematically expressed as Eq**. (3): **qe**

¼ qmax1 þKLKCLeCe ð3Þ

21**where qe is** milligrams **of** TET **adsorbed per** grams **of adsorbent, Ce**

is mil- ligrams of residual TET per liter of solution at equilibrium, KL is the Lang- muir affinity constant in units of (L/mg), and qmax

10**is the maximum adsorption capacity of the** adsorbent **with monolayer surface coverage**

in units of (mg/g) [31]. Freundlich equilibrium isotherm is

10**used to describe the multilayer adsorption with the interaction** between **adsorbed molecules. Freundlich model is represented**

in mathematics forms as Eq. (4): qe ¼ K FCe1=n ð4Þ (

24mg/g)(L/mg)−1/n and 1/n is

a heterogeneity factor that has no units (di-

5where KF is the measure of Freundlich adsorption capacity in units of

mensionless). For favorable adsorption, the

3value of n must fall between 1 and 10

[33]. Fig. 2. Illustration of adsorption of TET@10N1R and TET@20N1R. Impurities (e.g., sugars, alkaloid, and phenolic) from the rarasaponin-crude-extract were not illustrated for simplification purposes. Fig. 3. Adsorption isotherms of TET@10N1R (a, b), TET@20N1R (c, d) with

12Langmuir and Freundlich fittings. The adsorption isotherm profile of

TET@NCC is

12presented in the Sup- plementary data Fig

. S6, while TET@10N1R and TET@20N1R are shown

14in Fig. 3. The parameters of the two models are summarized in Table 1. The

adsorption mechanism can be studied from the adsorption iso- therm model.

17Langmuir isotherm assumes a monolayer coverage on a homogeneous surface with a particular adsorption site

, while Freundlich isotherm assumes that the adsorbates form a multilayer with interactions between the adsorbed molecules [34]. Both models can predict well the maximum adsorption capacity of TET onto the adsorbent under study. Based on the value of the correla- tion coefficient (R2), it was found

19that the Freundlich equation gives a slightly better fitting than the Langmuir

equation for all adsorbent Table 1 The parameters of Langmuir and Freundlich models for the adsorption system of TET onto NCC, 10N1R, and 20N1R. T (°C)

23Langmuir Freundlich KL (L/mg) qmax (mg/g) R2 KF (mg/g)(L/mg)−1/n n

R2 TET@NCC 30 0.0102 45 0.0175 60 0.0175 TET@10N1R 30 0.1523 45 0.1285 60 0.1503 TET@20N1R 30 0.1307 45 0.1660 60 0.2339 11.9440 0.9933 11.2567 0.9803 13.9675 0.9910 13.5289 0.9880 15.7013 0.9756 16.4692 0.9896 15.2738 0.9885 16.4783 0.9896 18.1089 0.9916 0.5033 1.8529 1.0104 2.3446 1.1830 2.2746 7.0921 7.6631 6.8120 5.8041 7.6764 6.2946 6.7777 5.9770 7.9055 6.4674 9.3992 6.9949 0.9941 0.9826 0.9921 0.9902 0.9825 0.9921 0.9940 0.9936 0.9938 systems. This indicates

19**that the adsorption occurs on the** non- homogeneous **surface of**

adsorbents. The arise of in-homogeneity is due to the random charge distribution and uneven distribution of rarasaponin on the adsorbent surface. The calculated maximum adsorp- tion capacity (qmax) indicates that 20N1R can adsorb more TET, followed by 10N1R and NCC; it suggests that the addition of rarasaponin provides more adsorption active sites. The higher adsorption capacity of 20N1R than 10N1R is influenced by the activity of rarasaponin, as illustrated in Fig. 2. Higher rarasaponin concentration, in 10N1R, causes a decrease in adsorption. In 10N1R, the excess rarasaponin molecules tend to form surfactant aggregations called micelles. These micelles interfere with the interaction between adsorbate and adsorbent; the micelles capture TET molecules and keep them hovering in solution so that the adsorp- tion capacity of the adsorbate decreased. While at 20N1R, there are enough NCC particles to accommodate the rarasaponin molecule on its surface; thus, rarasaponin can act as hands which helps in capturing TET molecules and supports adsorption. This argument also supported by the measured surface charge by zeta potential analyzer. 20N1R sam- ple shows a more negative surface charge than 10N1R; indicates that the more considerable amount of rarasaponin is attached on its surface than on 10N1R. Rarasaponin itself has a negative zeta potential, that is −3 so that the presence of rarasaponin contributes to the more negative zeta potential of the samples. The effect of temperature was also inves- tigated in the adsorption isotherm. The increase in temperature pro- motes the uptake of TET onto the adsorbents. This indicates that the adsorption of TET onto NCC, 10N1R, and 20N1R is endothermic. 3.4. Adsorption kinetic study Adsorption kinetic is the rate of adsorbate adsorbed onto the surface of the adsorbent. Several kinetic models are available

22**to represent the adsorption kinetic** data, such as **pseudo-first**-order **and pseudo- second-order**. Both models **are the most** commonly used **models**

to pre- dict the behavior of the liquid phase adsorption. The mathematical

16**form of the pseudo**-first-**order kinetic can be expressed as**

: ddqtt ¼ k1ðqe−qtÞ ð5Þ By integrating the equation above, the

11**final form of pseudo**-first- **order is**: qt ¼ qe 1− **e**

−k1t h i ð6Þ

15**where qt and qe are** milligrams of TET **adsorbed per** grams **of adsorbent at time t** (min) **and at equilibrium** respectively, **and k1 is the rate** con- stant of **the**

pseudo-first-order fitting in units of (min−1). While the mathematical

16**form of the pseudo-second-order kinetic can be expressed as**

: ddqtt ¼ k2ðqe−qtÞ2 ð7Þ By integrating the equation above, the

11**final form of pseudo-second- order is**

: qt ¼ qe 1 þqeqke2kt2t ð8Þ where k2 is the rate constant of pseudo-second-order adsorption fitting in units of (g/mg·min). k1 and k2 parameters show time needed by the system to reach the equilibrium [35,36]. As shown in Fig. 4, each kinetic adsorption system reaches equilib- rium in approximately 360 min. A plateau was observed afterward. The parameters obtained from the

11**pseudo-first and pseudo-second- order** fittings **are** given **in Table** 2. Based on **the** correlation coefficient (R2), **the**

two equations can represent the adsorption kinetics of TET an- tibiotic onto NCC, 10N1R, and 20N1R quite well. However, based on the qt values, it is convinced that pseudo-first-order can predict adsorption capacity better than pseudo-second-order. The qt obtained from pseudo-first-order is closer to the adsorption capacity of the experi- ment. The

21**pseudo-first-order model assumes that** physisorption con- trols **the**

adsorption process more than chemisorption — the time scaling parameter k1 and k2 in pseudo-first and pseudo-second-order measure the time needed to reach equilibrium. The time scaling param- eter is reduced on surfactant-modified NCC, and

17**the time required to** achieve the **equilibrium** condition **is**

longer. Table 2 Parameter of

2**pseudo-first order and** pseudo-**second-order for** TET **adsorption onto NCC**, 10N1R, **and**

20N1R. Adsorbents Pseudo first order Pseudo second order k1 qe R 2 k2 qe R 2 (min−1) (mg/g) (g/mg·min−1) (mg/g) NCC 0.0122 10N1R 0.0109 20N1R 0.0107 6.4020 0.9825 9.6084 0.9631 12.1760 0.9851 0.0014 8.1763 0.0008 12.3850 0.0006 16.0689 0.9747 0.9607 0.9806 3.5. A comparison study on the loading capacity of surfactant-modified NCC The addition of surfactants can provide additional active sites that promote the adsorption of adsorbate molecules that are dispersed in bulk solution. The enhancement of drug loading capacity by surfactant-modified NCC has been proven in some studies. Some of the studies

3**are summarized in Table** 3. It **can be seen** that **the**

surfactant-modified NCC has a higher drug loading capacity; for in- stance, only ~6 μg Docetaxel can be loaded on 1 mg of unmodified NCC, and ~40.5 μg Docetaxel can be loaded on 1 mg of CTAB-modified NCC [7]. Putro and group also showed that CTAB-modified NCC could load Paclitaxel 50-times higher than the unmodified NCC. In this work, the addition of rarasaponin also gives an enhancement in the loading capacity of TET, which is 1.12-times and 1.30-times higher for 10N1R and 20N1R, respectively. The enhancement in loading capacity provided by rarasaponin is much lower compared to CTAB, SDS, or Tween 20. This is because the extracted rarasaponin from Sapindus rarak still contains other crude compounds (impurities), other than rarasaponins, which is typical for many plant extracts [37,38]. As mentioned by Karim = and Azlan, Sapindus rarak pericarp contains many bioactive compounds such as raraoside, rarasaponin, saponins, acyclic sesquiterpene glycosides, and hederagenin [39]. A qualitative study of Sapindus rarak water extract showed positive results for the presence of compounds other than rarasaponin, namely flavonoids, alkaloids, tannins, and polyphenols [39,40]. The presence of impurities can interfere with the interaction of TET molecules with rarasaponin and NCC. Nevertheless, rarasaponin as a natural surfactant can be more beneficial, especially in terms of en- vironmental friendliness. In the term of biocompatibility, it should be noted that surfactant induced cytotoxicity in healthy cells if used at a high concentration. As demonstrated by Putro et al., good biocompati- bility is still maintained at Tween 20 concentration of 10 μg/mL, where Tween 20 only induces ~15% 7F2-cells (mouse osteoblast cells) death after 24 h; while at concentrations higher than 25 μg/mL, ~25% Fig. 4.

2**Adsorption kinetics of** TET **onto NCC**, 10N1R, **and** 20N1R **with** (A) **pseudo-first-order** fitting **and** (B) pseudo-**second-order**

fitting. Table 3 Comparison of drug loading capacity on unmodified and surfactant modified NCC. Modifying agent Drug Drug loaded (μg/mg) Ref Comp.a Conc. Unmodified Modified CTAB 12.9 mM CTAB 15 mM SDS Tween 20 CTAB 0.4 g/L Rarasaponin 0.5–1 g/L Docetaxel Paclitaxel Etoposide Paclitaxel Luteolin Luteoloside Tetracycline 6b 3.5b 1.3b 1.3b 1.2b 1.3b – – 13.97 40.5b 42b 25b 65.5 41b 28b 12.9 56.9 16.47 (10N1R) 18.11 (20N1R) [7] [15] [16] This study a CTAB = cetyltrimethylammonium bromide, SDS = sodium dodecyl sulfate. b Approximated value based on the presented graphical (curve) data in the literature. Table 4 Thermodynamic parameters of TET adsorption onto NCC, 10N1R, and 20N1R. Adsorbents ΔG° (kJ/mol) ΔH° (kJ/mol) ΔS° (J/mol·K) 30 °C 45 °C 60 °C NCC 5.20 10N1R −8.69 20N1R −8.23 4.76 3.28 −6.58 −10.17 −10.55 −13.68 24.41 62.88 5.36 43.51 46.65 180.71 cell death is observed. In this study, the rarasaponin extract used was much lower (0.5–1 μg/mL) so that good biocompatibility could still be expected [15]. Moreover, Morikawa and co-researchers also show that purified Sapindus rarak extract (30–100 mM) has good biological activ- ity, which is induced cytotoxicity on tumor necrosis in L929 cells [41]. A study by Faysoon also noted that Sapindus rarak extract induces moder- ate cytotoxicity against human gastric carcinoma, with IC50 values of 5.55 μg/mL [42].

24**3.6. Thermodynamic parameters** of **the** adsorption The **thermodynamic**

parameters, including the

26**changes in the** stan- dard **Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated by**

Eqs. (9) and (10): ΔG°¼−RT lnKD ð9Þ ln K D ¼ −ΔRHT ° þ ΔS ° R ð10Þ Table 5 Parameters of pseudo-first order and pseudo-second order of TET@20N1R desorption. pH

25**Pseudo-first order** k1D (**min−1**) qeD (**mg/g**

) R2 3 7 pH 0.1075 0.1597 Pseudo-second order 3.0377 7.7903 0.9078 0.9673 k2D (min−1) qeD (mg/g) R 2 3 7 0.0134 0.0105 4.9699 11.3466 0.9014 0.9589

18**where R is the universal gas constant (8.314 J/mol·K), T is** the tempera- ture **in** units of (**K**), and KD is **the**

distribution coefficient. Values of ln KD were determined from the regression of ln (qe/Ce) versus qe. Subsequently, the plotting of ln KD versus 1/T (as shown in Supplementary data Fig. S7) gives the value of ΔH° (slope) and ΔS° (intercept) [43,44]. The calculated thermodynamic parameters are listed in Table 4. A positive ΔG° value of adsorption of TET@NCC implies a non- spontaneous process. Meanwhile, a negative ΔG° value was observed for adsorption of TET@10N1R and TET@20N1R. This suggests that the addition of rarasaponin provides additional active sites that promote spontaneous adsorption. Positive values of ΔH° confirm the endother- mic nature of the adsorption [45]. Positive ΔS° values for all adsorbent indicates that there was an increase in the randomness of the solid- solution interface during adsorption. The positive ΔS° also suggests that the adsorption process is irreversible in the current adsorption pH, media, and temperature. 3.7. Desorption kinetic study The desorption kinetic study was performed for TET@20N1R since this system has the highest TET loading. The desorption of TET@ 20N1R was investigated in phosphate buffer medium at pH of 3 and 7; the rate of desorption was modeled

12**using the pseudo-first**-order **and pseudo-second-order** model. As shown **in Fig. 5, the**

TET desorption pro- file of 20N1R differs at pH 3 and pH 7. This indicates that the release of TET is pH-dependent. The release of TET continues, and the plateau was achieved after 14 h. The parameters resulting

25**from the fitting of** desorp- tion kinetics **are summarized in Table**

5, where qeD shows the amount of TET released at equilibrium time per mass of adsorbent. The desorption efficiency is determined by dividing the amount of desorbed TET with the amount of initial TET. The desorption efficiency at pH 3 is found to be 18.28%, which is lower than the desorption efficiency at pH 7, which is 55.49%. This is Fig. 5. Desorption kinetic of TET from 20N1R with (A) pseudo-first-order fitting and (B) pseudo-second-order fitting. because at pH b 3.3, the TET molecules present as cations while the surface of 20N1R is negatively charged; there is an attractive electrostatic force between two different-charged molecules that constrain the de- sorption.

9**At pH 7**, TET **molecules** present **as zwitterions, that** the **net charge**

of the entire molecule was zero. This results in the weakening of the electrostatic interaction between TET and 20N1R; hence, TET molecules can escape more easily. 4. Conclusion Rarasaponin extracted from the Sapindus rarak plant has been suc- cessfully incorporated to modify the surface of nanocrystalline cellulose (NCC) particles. Rarasaponin-modified NCC possesses better adsorption ability towards tetracycline (TET) than that of unmodified NCC. Adsorp- tion of the TET@NCC/Rara system proceeds endothermically, where

a physisorption mechanism is dominant. Thermodynamic studies re- vealed that the presence of rarasaponin promotes the spontaneity of ad- sorption. The desorption kinetics of TET from NCC/Rara showed higher desorption efficiency at pH 7. TET loading onto NCC can be improved with such low rarasaponin concentration (0.5–1 μg/mL); at this concen- tration, good biocompatibility of rarasaponin (crude extract) can be expected. CRediT authorship contribution statement Vania Bundjaja: Investigation, Formal analysis, Writing - original draft. Tirta Mutiara Sari: Investigation, Formal analysis. Felycia Edi Soetaredjo: Funding acquisition. Maria Yuliana: Writing - review & editing. Artik Elisa Angkawijaya: Writing - original draft. Suryadi Ismadji: Funding acquisition. Kuan-Chen Cheng: Writing - review & editing. Shella Permatasari Santoso:

6**Writing - original draft**, Funding acquisition, **Writing - review & editing. 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**. Acknowledgment **Financial support** from **the National** Taiwan University of **Science**

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13**Appendix A. Supplementary data Supplementary data to this article can be found online at https://doi. org/10.1016/j.molliq**.2019.112433. **References**

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