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J. Idn. Chem. Soc. 2020, 03(1), 59-67 FULL PAPER Citric Acid-Crosslinked Cellulosic Hydrogel from Sugarcane Bagasse: Preparation, Characterization, and Adsorption Study Maria Melania Golora, Dessy Rosmaa, Shella Permatasari Santosa*,b, Felycia Edi Soetaredjoa,b, Maria Yulianaa, Suryadi Ismadjia,b, and Aning Ayucitraa aDepartment of

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bDepartment of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan *Corresponding Authors: shella_p5@yahoo.com (Tlp. +62-3138-9126-4; Fax +62-3138-9126-7) Abstract In this work, citric acid (CIT) is proposed as a harmless alternative to epichlorohydrin (ECH) for crosslinking in the synthesis of cellulose hydrogels. Sugarcane bagasse was utilized as a source of cellulose fibers. Cellulose fibers were disintegrated using the solvent-dissolution method before forming a gel-like solution. Subsequently, CIT was added to initiate crosslinking, and the behavior was evaluated by adding various amounts of citric acid (0, 20, 30, and 40 wt%). Cellulose hydrogel with a good mechanical strength (10 mm penetration depth) was obtained from crosslinking using 40 wt% of CIT (HCIT-4), which is comparable to ECH-cross-linked hydrogel (HECH) that has a penetration depth of 8 mm. A proper amount of CIT molecules allows the crosslinking of the cellulose fibers into the hydrogel. The FT-IR analysis reveals a C-O- C band blue-shifting for HCIT-4 compared to HECH, with a gap difference of 82 cm⁻¹. The crystallinity from XRD patterns of HCIT-4 is comparable to that of HECH, which confirms that CIT can be used as a substitute for ECH. The adsorption ability was evaluated against methylene blue dye, the isotherm and kinetic adsorption models for the adsorption system were determined. Freundlich and pseudo-second-order models correlate well to isotherm and kinetics data, suggests that the adsorbent possesses heterogeneous surface sites which adsorption controlled by chemisorption. The prepared HCIT-4 was able to remove 24.88 mg methylene blue/g of the hydrogel at 70 °C, meanwhile HECH only able to remove 12.01 mg/g. The adsorption capacity was increased when adsorption temperature increased, suggesting endothermic behavior. A hydrogel material prepared by using cellulose polymer. Citric acid was used as the “green” crosslinker, instead of toxic compound epichlorohydrin. The prepared hydrogel has a porous cross-sectional morphology. The hydrogel is shown a potentiality in adsorption of dye, such as methylene blue. This ability of hydrogel can be very useful in wastewater management. Article History: Received: 25 March 2020, Revised 14 April 2020, Accepted 15 April 2020, Available Online 27 April 2020 <https://dx.doi.org/10.34311/jics.2020.03.1.59> Content from this work may be used

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Keywords: Adsorption, Cellulose, Citric acid, Crosslinking, Hydrogel Acknowledgment The authors are grateful to the Widya Mandala Surabaya Catholic University for the financial support of this work through an LPPM research grant 0657/WM01/N/2019. This work is also supported by the National Taiwan University of Science and Technology through joint research collaboration. Introduction Utilization and modification of biomass-waste containing cellulose into more valuable materials have been widely developed by engineers [1,2]. Sugarcane bagasse, a biomass waste, is a potential source of cellulose; it is known to contain 46 g cellulose, 24.5 g hemicellulose, and less than 20 g lignin per 100 g dry weight [2]. Sugarcane bagasse abundantly found in Indonesia. Sugarcane bagasse is produced in large quantities by many sugar factories. For instance, as many as 870,509 (in 2017) and 1,082,200 (in 2018) tons of sugarcane are processed by one sugar mill located in Mojokerto (East Java, Indonesia) per year. Plenty of sugarcane is processed by only one sugar mill, leaving some sugarcane bagasse available to be utilized. In this work, sugarcane

bagasse was utilized as a raw material for preparing hydrogel. Cellulose dissolution and crosslinking are the two fundamental steps in the preparation of cellulose hydrogels [3,4]. The presence of hydrotropic substances (e.g. urea) helps to prevent the recovery of cellulose fibers; thus, leads to the destruction of the supramolecular structure of cellulose, and eventually, cellulose dissolves. Crosslinking of dissolved cellulose is performed by the addition of a crosslinking agent, usually epichlorohydrin (ECH). The crosslinking between dissolved cellulose fibers occurs through nucleophilic substitution reaction [5,6]. Unfortunately, ECH is categorized as a dangerous carcinogenic compound [7]; thus, it is not safe for health and is not environmentally friendly. Highlighting the drawback of ECH, citric acid (CIT) was introduced as an alternative cellulose crosslinking agent. Many studies show the ability of CIT in promoting the cellulose crosslinking [8-11]; however, the effect CIT addition to the properties of hydrogel and its adsorptive ability is scarcely reported. The effect of the amount of CIT addition on the hydrogel properties was investigated. Hydrogel properties, i.e., mechanical strength, surface structure, functional groups, and crystallinity pattern are evaluated. The proposed application of hydrogels prepared in this work is their use in removing dye (methylene blue) from water. In this work, the preparation of cellulose hydrogel by using CIT as a crosslinking agent was demonstrated. The effect of CIT concentration on the formation of hydrogel was evaluated. The physicochemical properties of CIT-crosslinked hydrogels were compared to the ECH-crosslinked hydrogel; this is to demonstrate that CIT can be used as ECH substitute as a crosslinking agent. Nevertheless, the potential application of the CIT- hydrogel in removing methylene blue in aqueous solution was investigated. The application was studied in a single-batch adsorption system. Experimental Section

Sugarcane bagasse was obtained from the local market in Surabaya, East Java, Indonesia. Sodium hydroxide (NaOH, 97% purity) and sodium hypochlorite (NaOCl, 6 – 14% active chlorine) were obtained from Merck, Germany. Urea (CO(NH)₂, 98% purity), sulfuric acid (H₂SO₄, 95%

1purity), and epichlorohydrin (C₃H₅ClO, 98% purity) were obtained from Sigma Aldrich, Germany

. Analytical grade methylene blue dye (C.I. 52015, 82% dye content, $\lambda_{\text{max}} = 664 \text{ nm}$) and citric acid (C₆H₈O₇, 99.5% purity) were purchased from Sigma Aldrich, Germany. Extraction of cellulose from sugarcane bagasse Sugarcane bagasse (content: 45.24% cellulose, 25.36% hemicellulose, 10.03% lignin, 18.18% water, and 1.19% ash) was washed using tap water to remove the dirt. The bagasse was then cut into small pieces ($\pm 5 \text{ cm}$) and then dried in a 70 °C oven for 2 days. Dry bagasse was crushed into smaller sized particles. Hemicellulose content was reduced by soaking 5 g of dried bagasse in 100 mL of 10% (v/v) sulfuric acid for 10 min. Delignification was then performed to reduce the lignin content, and this step was done by soaking 5 g of acid-treated bagasse in 200 mL of 20% (w/v) NaOH for 2.5 h at 100 °C. The crude pulp was bleached using 1% (v/v) sodium hypochlorite solution for 3 h; followed by washing using deionized water and drying in a 100°C oven for overnight. The crude pulp (dried) was found to contain 83.68% cellulose, 5.44% hemicellulose, 6.05% lignin, 4.18% water, and 0.65% ash. Synthesis of hydrogel The solvent for cellulose dissolution was prepared by combining 7 g NaOH and 12 g urea, water is then added until the total solution weight is 100 g. 6 g of prepared crude pulp was then added to the 100 mL of the solvent. The crude pulp was dissolved by stirring the viscous solution vigorously for 1 h at a temperature of 30 °C. Different amount of CIT (0, 20, 30, and 40 wt%) was then loaded into the dissolved pulp, and then further stirred for 3 h at 70°C. The mixture was then subjected to 2 freeze- 60 thawing cycles before obtaining the hydrogel; the cycle was freezing at -20 °C for 3 h, and thawing at 30 °C for 3 h. The hydrogel was cut into 2 cm square, and freeze-dried. The dry hydrogel mass is $\pm 0.5 \text{ g}$. Figure 1 shows the synthetic pathway of the CIT-crosslinked hydrogel. In the first step, the presence of a hydrotropic solvent induces the hydrogen bond disruption of cellulose [3,4,12]. The disrupted sites of cellulose are vulnerable to nucleophilic attacks; these sites are the target of modification (crosslinking) in the next step [13]. In the second step, nucleophile-electrophile interactions occur due to the presence of CIT [5,6]. This interaction leads to the crosslinking of cellulose fibers to form three dimensional hydrogel networks. Figure 1. The synthetic pathway of cellulose hydrogel using CIT as the crosslinking agent. Adsorption study The adsorption isotherm was

performed by preparing a series of the bottle containing 0.05 L of methylene blue at various concentrations (50, 75, 100, 150, and 200 ppm), methylene blue diluted from a concentrated dye stock solution (500 ppm). One dry hydrogel block (± 0.5 g) was added to the flask. Adsorption was then carried out for 6 h at 30, 50, or 70°C. The equilibrium amount of adsorbed dye (QE, mg/g) was calculated according to Equation (1). $(C_i - C_f) V = m \times Q$ where C_i

6 and C_f , respectively, **are the initial and final concentration** of methylene blue **in mg/L; m is the mass of hydrogel (g); V is the total volume**

(L). The kinetics adsorption was carried out at a thermostatted condition of 30 °C. The kinetics system was studied at three different initial methylene blue concentrations of 50, 100, and 200 ppm. Five dry hydrogel blocks were added to each system. The residual dye concentration was measured at specified time intervals. The residual

4 amount of dye adsorbed at the given time interval (Q_t , mg dye/g adsorbent) was

determined using the Eq. (1), with the equilibrium term changed to time (t, min). Characterizations The surface morphology of the hydrogel sample was obtained in the form of SEM (JEOL JSM-6500F field emission SEM, Tokyo, Japan). The

1 Bruker D2 Phaser X-ray diffractometer

was used to obtain the crystalline pattern of the samples. The surface functional groups of the samples

1 were collected in transmission mode (%T) using a Bio-Rad FTS-3500 GX spectrometer

. The digital photographs were taken by using a Canon digital camera Powershot G5X. BET surface area of the hydrogels was determined using the nitrogen sorption method in an ASAP 2020 Micromeritics analyzer. The mechanical strength of the hydrogel was shown as the penetration depth, which measured using a universal penetrometer (model H-1310, with a blunt tip of a truncated cone). The water retention capacity was determined using the gravimetric method. Freeze-dried samples were soaked for 2 days in distilled water at room temperature. The surface of the soaked sample was blotted, and the weight was recorded using an analytical balance; this is the wet weight (wwet). The sample

1 was then dried in an oven (110°C). The dry sample was

weighed, and the weight was recorded as the dry weight (wdry). The water retention capacity was then calculated using Equation (2). $w\% - w\%_0 = w\% + w\% \times 100$ (2) 5 2 8 Results and Discussion In this work, several hydrogels from sugarcane bagasse cellulose have been prepared using CIT as the crosslinker. Hydrogels were prepared by adding different amounts of CIT (0, 20, 30, and 40 wt%), the hydrogels are coded as HCIT-0, HCIT-2, HCIT-3, and HCIT-4, respectively. A cellulose hydrogel using 5 v% ECH as a crosslinker (regular crosslinker for cellulose hydrogel) was also prepared for comparing characteristics; the hydrogel is coded as HECH. Characterization of the hydrogels The amount of CIT added as a crosslinking agent influences the formation of hydrogels and their degree of friability. HCIT-0, which is

prepared without the addition of CIT does not form a hydrogel; only cellulose slurry was obtained (inset Figure 2B). An addition of 20% CIT (HCIT-2) leads to the formation of a hydrogel with a very fragile network (inset Figure 2C). HCIT-2 is ready to dishevel into cellulose pulp after being put into water. The addition of 30% CIT (HCIT-3) results in a hydrogel that is less fragile than HCIT-2. Only a small portion of HCIT-3 (inset Figure 2D) is disheveled when put in water. An addition of 40% CIT in the formation of HCIT-4 (inset Figure 2E) produces a hydrogel whose texture is comparable to HECH (inset Figure 2A). HCIT-4 can preserve its shape, without disheveling, when put in water. HCIT-3, HCIT-4, and HECH have penetration depths of 12.2, 10, and 8 mm, respectively. HCIT-4 has better mechanical strength than HCIT-3; but has lower mechanical strength than HECH. Figure 2. SEM micrographs of hydrogels prepared from sugarcane bagasse as a cellulose source. (a) HECH, (b) HCIT-0, (c) HCIT-2, (d) HCIT-3 (right top figure shows morphology in other parts of the sample) and (e) HCIT-4. The inset figures are corresponding to the digital photograph of the hydrogel. Porous cellulose network morphology cannot be observed for HCIT-0; only clumps of cellulose fibers were found in HCIT-0 (Figure 2B). Similar morphology was observed for HCIT-2; cellulose fibers were also clumping (Figure 2C), thereby inhibiting the formation of a porous network. The porous network begins to be observed for HCIT-3 (Figure 2D). However, scanning the sample image at another point revealed that there was cellulose clumping in some areas (inset Figure 1D). A porous network similar to HECH was obtained for HCIT-4 sample (Figure 2E). Although the addition of 40% CIT can form the hydrogel (HCIT-4), but its physical properties are more inferior than HECH. HCIT-4 is only able to retain 160% of the water from its dry weight, while HECH can retain up to 178%. HCIT-4 is also lower in the specific BET surface compared to HECH, which is 1.79 m²/g for HCIT-4 and 2.12 m²/g for HECH. The hydrogels were possessing of the macroporous structure as suggested by the BET measurement. Characteristic bands of surface functional groups of cellulose, HCIT-4, and HECH were analyzed using FTIR analysis; no significant differences were observed from the bands (Table 1). All characteristic bands show only slight shifts, with the difference in the wavenumber (Δ) between 3 to 29 cm⁻¹. The only band for C-O-C stretch showed a more significant gap ($\Delta = 82$ cm⁻¹), the band was found at 1018 cm⁻¹ for HCIT-4 and 1100 cm⁻¹ for HECH. Table 1. Selected FTIR functional groups of the hydrogels. Assignments C-O-C stretch O-H or C=O bending Wavenumber (cm⁻¹) Cellulose* HCIT-4 HECH 1021 1018 1100 1602 1605 1600 C-H stretch 2904 2897 2910 O-H stretch 3339 3358 3397 *Cellulose prepared from sugarcane bagasse The crystallinity (XRD) patterns of HCIT-4 and HECH indicate the presence of cellulose types I and II (Figure 3). HCIT-4 and HECH have Bragg's peaks with strong intensity at $2\theta = 23^\circ$, and

1a broad (hump- like) peak at $2\theta = 13-18$

°; those peaks correspond

1 to the crystal planes of cellulose I

. A shoulder at $2\theta = 21^\circ$ was also observed which corresponds to a crystal plane of cellulose type II [14–16]. The crystallinity index (CI) calculation, based on the XRD results, reveals that HCIT-4 has a lower CI than HECH; that is 48.7% for HCIT-4 and 53.7% for HECH. The Ci of the studied hydrogel was comparable to the literature methylene blue onto HCIT-4 was driven by [4]. electrostatic interactions, which occur due to differences in charge between the molecules. HCIT-4 possesses hydroxyl groups that can be easily deprotonated and creates a negatively charged surface; meanwhile, methylene blue is known to behave as a cationic molecule in solution [18, 19]. The isotherm study of adsorption provides fundamental insights into designing an adsorption system [5, 20]. Two adsorption isotherm models were applied for data fitting. The data fitting shows a better correlation to the Freundlich model than the Langmuir model, as reflected by the higher related coefficient R² (Table 2). Figure 3. XRD pattern of HCIT-4 and HECH. Table 2. Parameters of the isotherm model for Effect of CIT on the formation of the hydrogel adsorption of methylene blue onto HCIT-4. The addition of a low amount of CIT (< 40 wt%) Temp. Freundlich model† does not accommodate

the formation of the network ($^{\circ}\text{C}$) KF (mg/g) n R2 SSE* so that hydrogels cannot be formed or only hydrogels (mg/L) $^{1/n}$ with a fragile texture are obtained. The addition of 30 0.9331 1.0718 0.9943 0.605 40% CIT has been demonstrated to form hydrogel 50 1.8441 2.0492 0.9939 1.161 with mechanical strength comparable to HECH. 70 4.2123 2.8090 0.9935 2.811 Obviously, at 0% CIT addition, no CIT molecule can Temp. Langmuir model \ddagger accommodate crosslinking between the cellulose ($^{\circ}\text{C}$) Qmax (mg/g) KL R2 SSE* fibers. At low CIT additions (20%) there are scant (L/mg) amounts of CIT molecules to function as crosslinking 30 18.0531 0.0113 0.9820 1.899 agents. At the addition of 30% CIT, the available CIT 50 21.8717 0.0187 0.9731 5.330 molecules are only sufficient to accommodate partial 70 28.1890 0.0381 0.9782 8.510 crosslinking; thus, the resulting hydrogel (HCIT-3) is *SSE is the sum square error that shows the differences between fragile. The addition of CIT > 40% has been tried. the observed and calculated data. The parameters of Freundlich However, the resulting hydrogel is fragile, like HCIT- and Langmuir were calculated by using the following equation: 2. The addition of CIT > 40% causes a significant $\ddagger Q! = K^{\prime} C!^{\#}/\%$ decrease in pH of the cellulose solution, thereby $\ddagger Q! = Q\&(\ \%\#+)!$ *!"" & reversing the dissolution of cellulose fibers and then where, KF and n are the constant indicating adsorption capacity and favorability, respectively. Qmax and KL are the maximum preventing crosslinking [17]. capacity and constant related to affinity, respectively. It was noted that a large amount of CIT (40 wt%) was required to prepare the hydrogel (HCIT-4), Furthermore, the SSE of Freundlich has lower which was much higher than the amount of ECH (5 values than Langmuir, indicating better data v%) needed to prepare HECH. This shows that CIT is correlation to the Freundlich model. The better fitting a crosslinking agent that is weaker than ECH. The to the Freundlich model suggests that HCIT-4 has weaker crosslinking by CIT is due to its acidic nature, heterogeneous adsorption sites. The heterogeneous which undeniably interferes with cellulose adsorption sites of the hydrogel were contributed by dissolution. However, despite the high need for CIT the presence of active adsorption sites by cellulose in hydrogel preparation, CIT is more and CIT molecules. CIT contributes to the carboxyl (- environmentally friendly than ECH. CIT is a non- COOH) sites, meanwhile, cellulose contributes to the carcinogenic compound and non-toxic, unlike ECH. hydroxyl (-OH) sites. The amount of methylene blue adsorbed onto HCIT-4 increases as the temperature Adsorption study on HCIT-4 against methylene increases (Figure 4), indicating endothermic blue behavior. HCIT-4 was able to adsorb 13.17, 18.00, and 24.88 mg dye/g at 30, 50, and 70 $^{\circ}\text{C}$, respectively. The potential adsorptive ability of HCIT-4 was Meanwhile, the highest adsorption capacity investigated against methylene blue. Adsorption of achieved by HECH is 12.01 mg of methylene blue per 63 g of the adsorbent, at 70 $^{\circ}\text{C}$. The adsorption capacity achieved by HCIT-4 is greater than several studied cellulose-based adsorbents against methylene blue dye. The adsorbent prepared by chemically modifying cellulose into microcrystalline cellulose only able to adsorb 4.14 mg/g [21]. However, it is much lower when compared to cellulose hydrogel composites. The acrylic acid-grafted cellulose hydrogel was able to adsorb 2104 mg methylene blue per g of the hydrogel [22]. Although the adsorption capacity of HCIT-4 hydrogels is not comparable with acrylic acid-grafted hydrogels, HCIT-4 has advantages in terms of its raw materials which are environmentally friendly and non-toxic. Figure 4. Adsorption isotherm of methylene blue onto HCIT-4 at 30, 50, and 70 $^{\circ}\text{C}$. Experimental data fitting to (a) Langmuir and (b) Freundlich models. Increased temperature induces deprotonation of surface functional groups in HCIT-4, causing surface charges to become more negative, and thus, allowing stronger interactions with cationic methylene blue molecules. The phenomenon of an increase in adsorption with an increase in

1 temperature can also be explained by the solubility of the adsorbate

[23]. Higher temperatures cause an increase in solubility of the adsorbate so that the mobility of the adsorbate becomes easier; as a result, interactions between adsorbate and adsorbents become more frequent. Table 3. Parameters of pseudo-first-order and pseudo-second-order kinetics for adsorption of methylene blue onto HCIT-4. Ci Pseudo-first-order \ddagger (ppm)* k1 (1/min) QE R2 (mg/g) SSE 50 0.0371 3.4663 0.9952 0.065 100 0.0448 4.6862 0.9926 0.158 200 0.0332 10.0363 0.9920 0.844 Ci Pseudo-second-order \ddagger (ppm)* k2 (g/mg QE R2 min) (mg/g) SSE 50 0.0094 4.2537 0.9952 0.058 100 0.0095 5.5660 0.9981 0.045

200 0.0026 12.6363 0.9927 0.730 *Ci represents the initial concentration of methylene blue The parameters were calculated by using the pseudo-first-order and pseudo-second-order equation (Lagergren 1898): $Q_t = Q_{\infty}(1 - e^{-k_1 t})$ (5) $Q_t = \frac{k_2 Q_{\infty}^2 t}{1 + k_2 Q_{\infty} t}$, (

86) where k_1 and k_2 are the pseudo-first-order and pseudo-second-order rate coefficients, respectively

The kinetics of the methylene blue adsorption system using HCIT-4 are modeled with pseudo equations. Lower SSE for pseudo-second-order shows that the adsorption kinetics data are more suitable to be modeled with pseudo-second-order (Figure 5, Table 3). The QE value calculated using the pseudo-second-order model is much closer to experimental data in isotherm. The better fitting to pseudo-second-order indicates that the chemisorption dominantly controls the adsorption [24–26]. The dominance of chemisorption was arising since the adsorbents possess deprotonable functional groups (i.e., –COOH and –OH). The deprotonation

3 of the functional groups was allowing the negative surface

charge of the hydrogels, and thus, the electrostatic interaction with the adsorbate occurs. Thermodynamic of methylene blue adsorption by HCIT-4

3 Thermodynamic parameters namely Gibbs energy change (ΔG , kJ/mol), enthalpy change (ΔH , kJ/mol) and entropy change (ΔS

, J/molK) are calculated to

7 provide information regarding the energy changes

[26,27]. Adsorption of methylene blue onto HCIT-4 is a spontaneous process, as 64 characterized by negative ΔG values (Table 4) [28]. The endothermic behavior of the adsorption system is supported by positive ΔH value. The random behavior of molecular interactions is shown by positive ΔS [24,26,28]; this confirms the heterogeneous nature of the adsorbent. Figure 5. Adsorption kinetics of methylene blue with different concentrations (50, 100, and 200 ppm) onto HCIT-4, at 30 °C. Experimental data fit to (a)

7 pseudo- first-order and (b) pseudo-second-order model. Table 4

Calculated thermodynamic parameters if methylene blue adsorption by HCIT-4. T Thermodynamic parameters (K) ΔG (kJ/mol) ΔH (kJ/mol) ΔS (J/mol K) 303 323 343 -3.6339 73.4118 18.5851 -5.1825 -6.5635 Conclusions Citric acid can be used as an alternative crosslinking agent for ECH. Hydrogels prepared by using CIT have more inferior properties compared to ECH-crosslinked hydrogels. However, CIT is more beneficial from the aspect of environmental safety. The CIT-crosslinked hydrogel shows the potential adsorptive ability to methylene blue. Authors contribution Data acquisition and interpretation: M.M.G. and D.R.; Analysis and Data Interpretation: M.M.G., D.R. and A.A.; Conceptualization: S.P.S. and M.Y.; Writing – Original Draft: M.M.G. and D.R.; Funding Acquisition: F.E.S. and S.I.; Writing – Review and Editing: S.P.S. and S.I. Conflict of Interest The authors declare no conflict of interest. References [1] L. J. Maschio, P. H. F. Pereira, and M. L. C. P. d. Silva, Preparation and Characterization of Cellulose/hydrous Niobium Oxide

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