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Investigation of the influence of crosslinking activation methods on the physicochemical and Cu(II) adsorption characteristics of cellulose hydrogels

4Shella Permatasari Santoso a, b, *, 1, Artik Elisa Angkawijaya c

, 1, Vania Bundjaja b, Alfin Kurniawan a, Maria Yuliana a, Chang-Wei Hsieh d, Alchris Woo Go c, Kuan-Chen Cheng e, f, g, h, Felycia Edi Soetaredjo a, b, Suryadi Ismadji a, b a Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia b Department of Chemical Engineering, National Taiwan University of Science and Technology, No. 43, Section 4, Keelung Rd., Taipei 10607, Taiwan

4c Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, No. 43, Section 4, Keelung Rd., Taipei 10607, Taiwan d Department of Food Science and Biotechnology, National Chung Hsing University

5145 Xingda Rd., South Dist., Taichung 40227, Taiwan

e

5Institute of Food Science and Technology, National Taiwan University, #1, Section 4, Roosevelt Rd., Taipei 10617, Taiwan f Institute of Biotechnology, National Taiwan University, #1, Section 4, Roosevelt Rd., Taipei 10617, Taiwan g Department of

5Medical Research, China Medical University Hospital, China Medical University, 91, Hsueh-Shih Road, Taichung 40402, Taiwan h Department of Optometry, Asia University, 500, Lioufeng Rd., Wufeng, Taichung 41354, Taiwan

ARTICLE INFO ABSTRACT Editor: Dr. GL Dotto Hydrogels represent an attractive soft material with promising applications in many fields. Conventional methods for hydrogel preparation typically involve heat curing either by water-bath (WB) heating or microwave Keywords: (MW) irradiation to facilitate crosslinking. However, a detailed investigation of the influence of WB- and MW- Cellulose hydrogel Epichlorohydrin mediated crosslinking process on the characteristics of hydrogels has been rarely reported. This work aims to Crosslinking evaluate the physicochemical properties of epichlorohydrin (ECH) crosslinked cellulose hydrogels prepared by Microwave irradiation WB and MW heating methods, including pore morphology, chemical composition, crystallinity, thermal stability, Water-bath heating and water absorption capacity. The results showed that MW heating could accelerate the crosslinking reaction Adsorption between cellulose and ECH to produce robust hydrogel, with a 3 min total irradiation time at 400 W compared to 2 h at 60 °C under conventional WB heating. The total utility cost to produce WBH is US\$ 0.052, which is 14 times higher than MWH (US\$ 0.004). The estimation of the total production cost of MWH on a large scale is US\$ 2.86 per kg. Moreover, the as-prepared MWH displayed outstanding performance in Cu(II) removal at 30 °C and pH 7, with a maximum adsorption capacity of 119 mg/g, respectively. The kinetic and equilibrium behaviors of Cu(II) ions on WBH and MWH were best described by pseudo-second order and Langmuir isotherm models, respectively. 1. Introduction Hydrogels (also referred to as superabsorbent polymers)

6are an important class of soft materials

that are constructed from three- dimensional (3D) linear or branched networks of crosslinked hydro- philic polymer chains, which are formed by either strong (i.e., covalent or ionic bonding) or weaker forces, such as van der Waals forces, hydrogen bonds, or hydrophobic interactions [1]. The high molecular weight and 3D network structure of hydrogel allow this material

6to absorb and store large volumes of water

(~100 times its dry weight) within its swollen matrix without dissolving [2,3], which is associated with the presence of abundant hydrophilic moieties, such as hydroxyl (– OH), carboxyl (– COOH), and amino (–NH₂)

groups [4]. Due to their exceptional swelling behavior, hydrogel materials have been widely applied in several areas,

15 **such as agriculture**, biomedical, **personal care products**, therapeutic delivery, **and water**

treatment [1,2,5].

6 **Hydrogels can be prepared from both synthetic**

(e.

6 **g., poly(acrylic acid)**, polyacrylamide, **poly(vinyl alcohol**

), etc.) and natural polymer * Corresponding author at: Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia.

1 **E-mail** addresses: **shella_p5@yahoo.com**

, shella@ukwms.ac.id (S.P. Santoso). 1 These authors have an equal contribution to this article. <https://doi.org/10.1016/j.jece.2021.106971> Received 25 August 2021; Received in revised form 9 November 2021; Accepted 5 December 2021 Available online 8 December 2021 2213-3437/© 2021 Elsevier Ltd. All rights reserved. Fig. 1.

15 **Illustration of the formation mechanism of hydrogel from cellulose**

fibers in the presence of ECH crosslinker. materials (e.g., cellulose and its derivatives, chitosan, alginate, etc.). In this regard, natural polymers are preferred over synthetic ones to fulfill the needs for renewable and sustainable technological materials, along with their inherent advantages, such as high abundance, low-cost, nontoxicity, biodegradability, and intrinsic biocompatibility [6–8]. Cellulose is one of the most commonly used polymer precursors to prepare hydrogels, due to its renewability and wide availability as a waste product of forestry and agricultural industries (e.g., bagasse, rice husk, corncob, etc.). In addition to its high natural abundance, the facile chemical modification of cellulose structure makes it adaptable for the preparation of a wide range of functional hydrogels with enhanced mechanical properties [9]. Cellulose hydrogels are traditionally prepared via the

1 **dissolution of cellulose fibers in** a hydrotropic alkali/**urea aqueous solution**

at low temperatures, typically below – 10 °C. In this regard, the

6 **dissolution of cellulose in common solvents**

at ambient temperature is difficult to realize

6due to the strong hydrogen bond network within crystalline cellulose

fibrils [10,11]. The addition of alkali can facilitate the breakdown of the hydrogen bonds between the cellulose monomers, thus enabling cellulose dissolution in water. Meanwhile, urea as a hydro-tropic agent plays an important role in interacting the hydrophobic moiety of cellulose with surrounding water molecules through van der Waals forces, thereby increasing the solubility of cellulose [11–13]. Once solubilized, the formation of 3D cellulose networks (or the hydrogel) is induced by adding crosslinker molecules (e.g., epichlorohydrin) and subsequently followed by thermal activation. Over the past few years, microwave (MW) irradiation has attracted considerable attention as an alternative energy source for rapid, selective, and homogeneous heating

28compared to the conventional heating modes by thermal conduction and convection

mechanisms. More recently, the MW heating technique has been adopted in hydrogel preparation [14–17], which

6can significantly reduce the time and energy consumption of

the crosslinking process without compromising the

29physical and chemical properties of the final product. However, the influence of the

MW-assisted

6crosslinking reaction of cellulose with epichlorohydrin (ECH

) on the physicochemical characteristics of the resultant hydrogels has remained relatively unexplored. Herein, we report a detailed study of the effect of two thermal activation methods, namely water bath (WB) heating and MW irradiation on the physicochemical properties, as well as swelling behavior of ECH-crosslinked cellulose hydrogels. The

6physical and chemical characteristics of the resulting hydrogels

were examined by various techniques, such as scanning electron microscopy (SEM), Fourier transforms infrared (FTIR) spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and atomic force microscopy (AFM). Moreover, techno-economic analysis and life cycle cost assessment of the hydrogels are presented. Furthermore, the application potential of the resultant hydrogel as an eco-friendly and adsorbent was evaluated for copper ion (

16Cu(II) removal from an aqueous solution. Detailed assessment of **the kinetics, equilibrium, and**

mechanism of Cu(II) adsorption by the hydrogel sorbents is also provided. Fig. 2. Schematic illustration of (a) WB heating and (b) MW irradiation on cellulose gel solution.

232. Materials and methods 2.1. Materials Teabag **filter paper (TFP) was** employed **as** the cellulose fiber **source**

and obtained

11from a local distributor in Surabaya, East Java, Indonesia

1Sodium hydroxide (NaOH, 96% purity) was obtained **from Yakuri Pure**

Chemicals Co., Ltd. Urea (CH₄N₂O, 98% purity), ECH (C₃H₅ClO, 98% purity), hydrochloric acid (HCl, 37%), 1,5-diphenylcarbazine (C₁₃H₁₄N₄O, 98% purity), ethanol (C₂H₆O, 95% purity), and copper chloride dihydrate (CuCl₂·2H₂O, 99% purity) were

6purchased from Sigma Aldrich, Singapore and used as received **without further purification. All aqueous solutions were prepared using ultrapure water**

with a resistivity of 18.2 MΩ·cm. 2.2. Preparation of cellulose hydrogels TFP as the cellulose source

1was soaked in water overnight and then shredded into pulp using a blender. Subsequently, the shredded pulp was collected **and oven-dried**

(105 °C) for 24 h. Dried pulp was then pretreated using a 0.5 M NaOH aqueous solution to remove impurities and thoroughly washed with water,

4followed by drying in an oven at 105 °C overnight. The

1dried pulp was finely pulverized **using a blender to**

reduce the fiber particle size and stored in a desiccator until further use. Cellulose hydrogels were prepared by adding 3 g of pretreated TFP pulp to a precooled (– 12 °C) aqueous solution containing NaOH (7 g), urea (12 g), and water (81 g). The mixture was then vigorously stirred for 30 min and the resultant

23solution was centrifuged at 3000 rpm for 3 min to

separate any undissolved material. Subsequently, 5 mL of ECH was added to the cellulose solution, stirred for 20 min, and then poured into a 10-cm Petri dish. The dish was

1then placed in a thermostatically controlled **water-bath** (Memmert WNB-45) **at 60 C**
for 20 min to facilitate **the**

crosslinking of cellulose polymer chains. Meanwhile, the MW-assisted crosslinking process was carried out using a domestic microwave-oven (Sampo RE-0711) operating at 400 W by applying three consecutive heating for 1 min each (3 min of total irradiation time). In the present experiments, the temperature and time for WB heating were selected based on a set of pre-experimental runs. It was found that a shorter heating time resulted in the formation of hydrogels that were not robust enough for molding, likely due to low degrees of crosslinking. After crosslinking, all the hydrogel samples were thoroughly washed with water to remove unreacted crosslinkers. The hydrogel samples were then cut into ~1 cm³ sized cubes with a razor blade and lyophilized overnight. Finally, the lyophilized samples were stored in a desiccator until further use. The as-prepared hydrogels by WB heating and MW irradiation are designated as WBH and MWH, respectively. 2.3. Characterizations of the hydrogels Scanning electron microscopy (

2SEM) analysis was performed using a JEOL JSM-6500 field emission SEM

at 10 kV. Prior to imaging, the

5samples were sputter-coated with a **thin Pd/Pt film using a JEOL JEC-3000FC**
auto fine **coater**

. Compositional analysis was performed using an Oxford energy dispersive X-ray spectrometer (EDS) attached to the SEM and the spectra were analyzed by the Oxford INCA software.

4X-ray diffraction (XRD) patterns were collected using a Bruker D2 Phaser X-
ray diffractometer (XRD) equipped with a Cu K α radiation source ($\lambda = 0.15418$
nm

).

1Surface functional groups of the samples **were analyzed**

Fig. 3. Morphology of ECH crosslinked cellulose hydrogels. (a, b) Top-view and (c, d) cross-section SEM images of WBH (left) and MWH (right) along with corresponding EDS elemental maps of C, O, N, and Na. The scale bars represent 100 μm . AFM topography images of (e) WBH and (f) MWH. The scan area for both images is 90 $\mu\text{m} \times 90 \mu\text{m}$. using attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy. The transmission

30 spectra were acquired in the wave-number range of 4000–500 cm^{-1}

2 using a Bio-Rad FTS-3500 GX

spectrometer with the spectral

2 resolution of 4 cm^{-1} . Thermogravimetric – analysis (TGA) was performed by a TA instruments TGA 550

20 from 30 to 600 $^{\circ}\text{C}$ with a ramp rate of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere

22 X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo VG Scientific ESCALAB 250 spectrometer equipped with a monochromatic Al $\text{K}\alpha$ X-ray source

($h\nu$ 1486.6 eV) and the obtained spectra were analyzed with the XPSPEAK41 software. Binding energies were calibrated using the C 1s peak of adventitious carbon at 284.5 eV. Atomic force microscopy (AFM) characterization was carried out using a Bruker Dimension ICON AFM system operating in mode and the data were processed by NanoScope Analysis software. Zeta potential measurements were carried out according to a previously reported procedure from Ibrahim et al. [18].

20 The equilibrium swelling ratio of the hydrogel samples was determined by

a gravimetric method following the procedure described in our previous work [11]. The Cu content in the postsorption hydrogel samples was analyzed by

8 inductively coupled plasma optical emission spectrometry (ICP-OES; Thermo Scientific iCAP 7000). 2.4

. Cu(II) uptake experiments The effects of pH and initial concentration on the removal efficiency of Cu(II) ions by WBH and MWH were studied using the batch method at room temperature ($\sim 30^{\circ}\text{C}$). For the pH study, a series of glass-stoppered Erlenmeyer flasks containing 25 mL of CuCl_2 solution (200 mg/L) was prepared and the pH

24 was adjusted to between 2 and 9 by either 0.1 N NaOH or HCl aqueous solutions. Subsequently, 0.2 g of hydrogel was added into each solution and

the mixture was incubated at room temperature under gentle shaking (

33100 rpm) for 8 h to reach equilibrium. The

19effect of initial Cu(II) concentration was evaluated in the concentration range of 5–500 mg/L

with an adsorbent dosage of 0.2 g and the initial pH value of 7. The residual Cu(II) concentrations in the solution were measured using a spectrophotometric method according to the procedure described by Turkington and Tracy [19]. The

14percentage removal and the equilibrium adsorption capacity (Q_e)

)

14were calculated according to Eqs. (1) and (2), respectively. %Cu removal

= $C_0 - C_f \times C_0$ 100% (1) $Q_e = C_0 - C_e \times V$ (2) Fig. 4. Characterizations of the as-prepared WBH and MWH. (a) ATR-FTIR spectra. (b) XRD patterns. The black vertical bars indicate the Bragg reflection peaks of cellulose I structure (JCPDS card no. 03–0226). The solid circle and star symbols represent the Bragg reflections of cellulose I and cellulose II in the hydrogel samples, respectively. (c) TGA traces recorded in N₂ atmosphere and the corresponding DTG curves (inset). (d) Swelling ratio in pure water at room temperature. Error bars represent standard deviations of the mean from triplicate measurements. Fig. 5. (a) XPS survey and high-resolution (

12b) C 1s and (c) O 1s

spectra of WBH and MWH together with the curve-fitting results.

13where C_0 , C_f , and C_e represent the initial, final, and equilibrium concentrations of Cu(II) ions in solution (mg/L), respectively, V is the volume of the metal solution (L), and m is the mass of the sorbent (g). For the

kinetic experiments, the same procedure as described above for the adsorption equilibrium (C_0

14200 mg/L, pH 7, and

adsorbent dosage (0.2 g) was followed except that aliquots of the metal solution were withdrawn at specified time intervals for analysis. The adsorption capacity at time t (Q_t) was determined by the following equation: $Q_t = C_0 - C_t \times V$ (3) where C_t is the concentration of Cu(II) ions in solution at a certain time (mg/L). The distribution coefficient (K_d), which reflects the affinity of the sorbent material toward heavy metal ions [20],

25 was calculated from the equation $\sqrt{[(C_0 - C_e)/C_e]}$ /m where both symbols and

units are the same as described above. Table 1 Utility costs in the laboratory-scale production of cellulose hydrogels by WB heating and MW irradiation methods. WB heating MW irradiation Electricity Power (W) Heating time (min) Electricity cost (US\$/kWh) Total electricity cost (US\$/batch) Water consumption (m³) Water cost (US\$/m³) Total water cost (US\$/batch) Total utility cost (US\$/batch) 2000 20 0.079 0.053 0.041 0.074 0.003 0.056 1100 3 0.079 0.004 – 0.074 – 0.004 a A single batch process afforded about 2.3 g of wet hydrogel or 1.67 g of dry gel after lyophilization. b Indonesia electricity and water prices as of March 2021, accessed from [www. GlobalPetrolPrices.com](http://www.GlobalPetrolPrices.com) with currency exchange rate 1 US\$ = 14,163.73 IDR (<https://www.globalpetrolprices.com/Indonesia/>, accessed date 27 October 2021). 3. Result and discussion 3.1. Formation mechanism of the WBH and MWH hydrogels The use of 7–9 wt% NaOH solution in combination with 2–4 wt% urea is known to facilitate the dissolution of cellulose [21]. However, repeated freezing-thawing cycles are required to reach a high degree of dissolution, making it impractical. Cai et al. have reported a way to diminish this drawback by altering the

35 mass ratio of NaOH:urea:water to 7:12:81

–Using this ratio, the dissolution of cellulose can be carried out without the need for freezing-thawing cycles. The dissolution of cellulose can occur rapidly by mixing the cellulose into the precooled solvent (i.e., below – 10 °C) at ambient temperature [22]. The

35 mass ratio of NaOH:urea:water of 7:12:81

was adopted to prepare the cellulose solution in this work. The illustrative mechanism of cellulose hydrogel formation is presented in Fig. 1. The process of cellulose hydrogel preparation was initiated by dissolving cellulose fiber in precooled hydrotropic solution mixture (i.e., alkali/urea, the alkali is commonly NaOH or LiOH) [21–27]; the use of NaOH is often more preferable owing to its low-cost and low toxicity [28]. The dissolution of cellulose occurs as the hydrogen bonds at the intra- and intermolecular cellulose chain are disrupted (Fig. 1, step i). The hydrogen bond disruption happened due to the formation of new hydrogen bonding between hydroxyl groups of cellulose and hydrotropic molecules of solvents (Fig. 1, step ii) [23,29, 30]. As a capping agent, the urea attaches to the hydrophobic moiety of cellulose and forms a hydrogen bond with water molecules. Furthermore, the presence of urea also helps in preventing the aggregation of cellulose [11,12,28]. The hydrogen disruption by NaOH/urea leads to the decreased hydrophobicity of cellulose and thus facilitates its dissolution in water. After the cellulose solution was obtained, ECH was added. The basicity of the NaOH/urea solvent system facilitates the Williamson etherification and oxalkylation between ECH and two adjacent cellulose chains (Fig. 1, step iii). The interaction between ECH and cellulose can be explained stepwise: before interacting with cellulose, the epoxide ring of ECH encountered an oxyanion attack. These oxyanions act as the nucleophile generated from the deprotonation of cellulose in the glycosidic residues [31]. The presence of NaOH in the system acts as

1a catalyst for the opening of the epoxide

ring and

1 causes detachment of the Cl atom from the epoxide group [32]. The

1 ring-opened ECH contains two electrophilic carbon atoms at its end, which are the

points of nucleophilic attack by oxyanions from the deprotonated cellulose [11]. To transform the crosslinked cellulose to hydrogel networks, an activation procedure through MW irradiation or WB heating was required [24]. In this study, two cellulose hydrogels were prepared via two Table 2 Overall cost estimate for scaled-up hydrogel production by MW irradiation method based on the LCCA approach. Scenario Unit Price Quantity and Total Cost Description (US\$) Units (US\$) Raw material cost Transportation cost (1) Manual collection Transportation cost (2) Mixing cost Heating cost Drying cost Chemicals Utility costs Energy loss 930.00a 420.00b 8.00c 75.00d 0.079 (electricity price per kWh)e 0.079 (electricity price per kWh)e 0.079 (electricity price per kWh)e 1350.00a,f 0.074 (water price per m³)e 0.079 (electricity price per kWh)e 1 ton biomass 1 ton 2 people per day 1 ton, 500 km 0.5 h, P = 0.5 kW (industrial mixing tank), load in 2 batches 0.05 h, P = 1.1 kW, load in 1 batch 3 h, P = 243 kW, load in 1 batch 1 ton of hydrogel 1 ton of hydrogel 0.05 h, P = 0.11 kW 930.00 Cellulose fiber from wood pulp 420.00 Import rate by considering net rate ocean freight port to port from China to Indonesia, with expedition time of 8 days. 16.00 2 people are required to transport the sample from port to facility. 75.00 Transportation of sample from port to facility. Logistic price for transporting up to 10 ton materials with distance up to 500 km. 0.003 Mixing of all raw materials, the mixing

34 parameters based on this work. The volume of the tank is

0.6

34 m³ and the power (P) is 0.5 kW

. 0.004 The heating process refers MW irradiation with the estimated cost described in Table 1. The microwave has 1816 kg (4000 lbs) capacity. 53.22 The drying process of hydrogel using a freeze dryer. The industrial freeze dryer capacity is 1.5 ton per batch. 1350.00 The chemicals consist of NaOH, urea, and ECH, with the amount based on this work. The water required for the reaction and washing the product, that is 1 m³ approximately. 0.0004 The main consideration is the power loss during the heating microwave. (continued on next page) Table 2 (continued) Scenario Unit Price Quantity and Total Cost Description (US\$) Units (US\$) Other – Total 2859.23 1 ton of hydrogel The estimated total cost of 1 ton of wet hydrogel. The estimated price per kg of wet hydrogel is US\$ 2.86. The heating cost (only) is US\$ 0.0003. 15.00 Power loss is estimated 10% of the required power. Considering additional cost manual filling material, pick-up, etc. activation procedures, namely WB at 60 C and MW at the power of ° 400 W. A total of 20 min WB activation is essential to ensure the complete crosslinking of WBH and cutting down the heating period may result in a partly unsolidified hydrogel (according to pre-experiment of this work). On the other hand, MW is shown to accelerate the time needed for hydrogel activation, where no more than 3 min of MW is required for solidifying the MWH. A graphical illustration of the WB activation mechanism was presented in Fig. 2a. The WB heating process can be considered a conventional heating method, where the heat source naturally comes from the mold surface and gradually seeps into the molecules via convection current [33]. This current allows the movement of the molecules, and eventually, the interaction between molecules occurs due to the collision. The heat transfer of WB heating starts from the surface of the material; the rate of heat flow to the bulk of the material is dependent on several factors such as specific heat, thermal conductivity,

and viscosity. Furthermore, the heat distribution from the WB is not homogenous, where more significant heat is distributed on the surface of the material and lower heat is distributed into the bulk of the material [34–36]. The non-uniform heat distribution by the WB heating method results in the requirement of a longer heating time to initiate the crosslinking reaction in the formation of a hydrogel. Meanwhile, in MW irradiation –As the molecules absorb the MW, the heating comes from two main mechanisms: ohmic heating and dielectric heating. Ohmic heating occurs from the oscillation of the free ions (e.g., Na from NaOH and Cl- from ECH); the oscillation triggers collision with + neighboring molecules and creates heat energy. Dielectric heating occurs due to the

28rotation of molecular dipoles as the molecules **attempt to align to the** oscillating MW **field**

; the alignment causes friction, creating heat energy [34–36]. The MW irradiation allows faster heating and uniform heat distribution on the surface and within the bulk of materials. The illustration of the heating process by MW irradiation is shown in Fig. 2b. The advantages of shorter crosslinking time during the cellulose hydrogel preparation by using the MW irradiation procedure have been reported in several works [14,37–39]. For example, Huber et al. showed that 20 and 10 min of MW heating (at 100 and 180 W, respectively) was required to set the cellulose hydrogel [37]. As a comparison, 20 min to 6 h was required to activate the linking of the cellulose-based hydrogel using the WB method [11,37,39]; e.g., Huber et al. show that 6 h and 2 h (at 50 and 60 °C) was required to prepare the solid cellulose hydrogel [37]; Zhang et al. reported that 3 h (at 60 °C) was required to obtain cellulose/multiwalled carbon nanotubes composite hydrogel [39].

3.2. Characterizations of the WBH and MWH The influence of the conventional WB heating and MW irradiation methods on the morphological features of the hydrogel samples were first elucidated by SEM. Fig. 3 shows the surface and cross-section morphology of the WBH and MWH. Both hydrogel samples exhibit a relatively rough surface and similar porous morphology, which is formed when the cellulose fibers are crosslinked into each other. AFM topography images of WBH (Fig. 3e) and MWH (Fig. 3f) corroborate the roughness of the hydrogel surfaces with root-mean-square roughness (Rq) of 2.44 and 2.41 μm, respectively. The mapping results indicate that both hydrogels have a similar distribution of C, O, N, and Na elements within their matrix. These results suggest that the thermal activation process, either by WB heating or MW irradiation, during the crosslinking reaction of cellulose chains with ECH does not significantly impact the morphology of the resultant hydrogels, which leads our further investigations on the chemical and swelling properties of the hydrogels. The strong and broad band centered at 3392.8 cm⁻¹ can be assigned to the O–H stretching vibrational mode engaged in hydrogen bonding. As can be seen in the spectra, compared with the TFP as a cellulose precursor, the broader and peak for WBH and MWH may indicate higher water retention in the internal structure of hydrogel materials, which could be attributed to the crosslinked cellulose network. The bands at 2885.5 and 1627.9 cm⁻¹ are related to asymmetric C–H and O–H bending –It was noted that the intensities of these two bands are much stronger for WBH and MWH compared to TFP, this could be ascribed to the incorporation of ECH crosslinker molecules and stronger H-bonding interaction of the hydrogels than the cellulose fibers [40]. Further evidence for the successful crosslinking reaction between ECH and cellulose fibers via the formation of ether linkages comes from the appearance of a vibrational band at 1363.7

11cm⁻¹, which corresponds to the symmetric **stretching of the C–O–C group**

at the ECH backbone [4]. The band associated with the C–O or C–C stretch of primary alcohol was observed at 1024.2, 1028.1, and 1030 cm⁻¹ for TFP, WBH, and MWH, respectively. The observed characteristic peaks were in good agreement with the reported literature related to the FTIR spectra of crosslinked cellulose [41–44]. The XRD patterns of TFP, WBH, and MWH are depicted in Fig. 4b. The TFP

exhibited a typical diffraction pattern of native cellulose (cellulose I) with reflection peaks at 2θ 14.9°, 16.4°, and 22.8°. These are reflections

1 can be assigned to the (110), (110), and (200) planes of the cellulose I crystal structure, respectively

(JCPDS card no. 03–0226). On the other hand, the WBH and MWH predominantly consist of cellulose II, as evidenced by the characteristic (110) and (020) diffraction peaks at 2θ of $\sim 20.1^\circ$ and $\sim 22.3^\circ$, respectively. The irreversible conversion

30 of crystalline cellulose I to cellulose II

allomorph via intracrystalline swelling and subsequent recrystallization can be attributed to the treatment of cellulose fibers with concentrated aqueous NaOH, also known as the mercerization process. This result is consistent with the previous studies; and, it occurs due to the hydroxyl anions of NaOH attack the primary cellulose wall, causing the disruption of the inter-molecular and intramolecular hydrogen bonding network and subsequent alteration in its crystallinity [45–47]. TGA profiles of the WBH and MWH are depicted in Fig. 4c, revealing two mass loss events

7 in the temperature range of 30–600 °C. A sharp weight loss of

57.1% and 55.6% for WBH and MWH, respectively, between 250 and 400 °C corresponds to the thermal degradation of crosslinked cellulose chains,

15 which is in good agreement with previous reports [48,49]. The

DTG curves (inset) indicate that both the hydrogel samples exhibit similar maximum decomposition temperature (T_{max}) at about 330 °C, suggesting that the crosslinking activation method either by WB heating or MW irradiation does not considerably affect the physical structure and the thermal stability of the resulting hydrogels. Time-dependent swelling behaviors of WBH and MWH in pure water Fig. 6.

Characterizations of the postsorption samples of WBH and MWH. (a, b) Top-view and (c, d) cross-section SEM images of the Cu(II)-loaded WBH and MWH, along with the corresponding Cu and Cl elemental maps. (e) ATR-FTIR spectra. (f) XRD patterns. Dotted lines in the ATR-FTIR spectra and XRD patterns correspond to the pristine hydrogel samples.

11 are displayed in Fig. 4d. As can be seen in

this figure, the absorption of water into the hydrogels occurs rapidly within the first 2 h, after which the swelling rate gradually slowed down and reached equilibrium after 16 h. The equilibrium swelling ratio of the WBH and MWH materials was determined to be 48.7 and 49.2 wt%, respectively. However, it can be noticed that the MWH sample, whose crosslinking reaction is facilitated by MW irradiation, shows faster swelling kinetics than the WBH counterpart. XPS analysis was conducted to provide more information about the elemental composition and the chemical nature of the functional groups on the WBH and MWH surfaces through analysis of the

12C 1s and O 1s core-level spectra. The

XPS survey and

12high-resolution spectra of C 1s and O 1s

are shown in Fig. 5. In survey XPS spectra, both the cellulose hydrogel samples show two prominent peaks at 284.5 and 531.5 eV, corresponding to carbon (C) and oxygen (O), respectively, along with a small Na 1s peak at 1070.5 eV. Calculation of the relative atomic concentrations of C and O elements from the survey spectra reveals that both WBH (C/O 1.94) and MWH (C/O 2.14) exhibit quite similar surface compositions. The C 1s XPS spectra of WBH and MWH (Fig. 5b) can be deconvoluted into three peaks at 283.9, 285.3, and 287.3 eV, corresponding to the sp²-hybridized carbon, C–OH, and C–O–C groups, respectively. These assignments are in good agreement with the peak fitting results of cellulose nanofiber [50] and cellulose/alginate monolithic hydrogel [51]. The high-resolution O 1s spectra of WBH and MWH in Fig. 5c can be fitted with two different carbon-oxygen functional groups, namely C–OH at 530.8 eV and C–O at 532.1 eV. All of the physicochemical measurements above indicate that the WBH and MWH samples exhibit similar characteristics. WBH and MWH have macroporous structures, with the primary elemental composition of C and O atoms. The main functional groups of the hydrogels are C–C, C–O, and C–OH. Comparison of FTIR spectra of WBH and MWH before and after adsorption. Wavenumber (cm⁻¹) Assignment

WBH Before	WBH After	MWH Before	MWH After	Assignment													
3394.7	3415.1	2881.7	2890.2	1626.0	1650.3	1361.7	1368.2	1028.1	1034.1								
30.4	3392.8	8.5	2885.5	24.3	1627.9	6.5	1363.7	6.0	1024.2	3425.3	32.5	2899.1	13.6	1653.4	25.5	1371.8	8.1
1033.2	9.0	O–H stretching	C–H stretching	O–H bending	C–O–C stretching	alkyl aryl ether C–O/C–C stretching	primary alcohol	a	The magnitude of wavenumber shifts in FTIR of the hydrogels before and after Cu(II) adsorption. b The peak assignment based on Ref. [53]								

14C–O–C, C–OH, and C–O

. The presence of the C–O–C bond can be attributed to the crosslinking of the cellulose by the ECH. These results imply that WB and MW activation method results in hydrogels with similar physicochemical properties; thus, both methods can be interchangeably used to prepare the hydrogel. Nevertheless, as discussed in the next section, the MW irradiation technique can be more practical by considering a shorter treatment period and energy consumption for the crosslinking process. 3.3. Economic feasibility analysis The economic analysis result demonstrates the practical benefit of the MW irradiation technique over conventional WB heating for hydrogel preparation. Table 1 shows the comparison of utility costs in the laboratory-scale synthesis of cellulose hydrogel using WB heating and MW irradiation processes, including process water and electricity consumption. The results show that the total electricity cost (only) for WB heating is more than 13 times higher than that of MW irradiation, which is mainly contributed by the longer heating time and greater power consumption of the process. Moreover, the requirement of water as a heat transfer fluid in the WB heating process incurs a higher utility cost. The total utility cost for hydrogel production using the conventional WB heating method was found to be 0.056 US\$/batch, which is about 14 times higher than the MW irradiation (0.004 US\$/batch), thus signifying the advantages of the latter technique in terms of low-cost and energy-saving. To evaluate the economic feasibility of the MW irradiation method for the scaled-up production scenario, we estimated the overall production cost of 1000 kg wet hydrogel (or about 767 kg of dry hydrogel) as the basis using life cycle cost analysis (LCCA). LCCA can be used as a basic reference for the evaluation and simulation of methods in more in-depth research in the future [52]. In this engineering-economic analysis approach, the overall cost estimation is based on the sum of several cost elements, such as raw material and its handling, transportation, utilities (i.e., electricity and

water), processing, chemicals, and others. As shown in Table 2, the overall production cost for 1 kg of wet cellulose hydrogel using the MW method is about US\$ 2.9. This table shows that the chemical auxiliaries (i.e., NaOH, urea, and ECH) and raw material represent the largest contributors to the overall cost, which accounts for 33% and 47% of the total cost, respectively. On the other hand, the utility cost associated with the power consumption of MW irradiation Fig. 7. (a) Zeta potential vs. pH curve for WBH and MWH sorbents. (b) pH

8effect on the Cu(II) removal by WBH and

MWH (Conditions:

25CO = 200 mg/L, T = 30 °C, and adsorbent dose = 0.2 g

). Effect of initial concentration on the (c) equilibrium adsorption capacity and (d) Cu(II) removal efficiency of WBH and MWH (Con- ditions: pH = 7, T = 30 °C, and adsorbent dose = 0.2 g). Fig. 8. Adsorption kinetics curves of Cu(II) on WBH and MWH and the kinetic plots of (a) P1O, (b) P2O, (c) Elovich, and (d) IPD models. shows a negligible contribution (0.0014%) to the overall cost, thus highlighting the low-cost and energy-saving nature of this method. In this regard, a significant cost reduction for hydrogel production can be achieved by utilizing local agricultural and industrial wastes as low-cost cellulosic feedstock, as well as building the facility closer to the existing infrastructure to minimize transportation and material handling costs. 3.4. Adsorption behavior of Cu(II) ions onto WBH and MWH 3.4.1. Characterizations of the Cu(II)-loaded hydrogels The characterizations of the postsorption WBH and MWH samples were performed by SEM, XRD, FTIR, and XPS techniques to gain detailed insight into the Cu(II) uptake mechanism. SEM images along with the EDS elemental maps of the Cu(II)-loaded WBH and MWH are depicted in Fig. 6. As can be seen, the surface and pore cross-section morphology of the hydrogels remain intact after the sorption process, demonstrating the robust stability of the materials. The EDS mapping revealed the uniform distribution of Cu signal on the surface and throughout the cross-section of the hydrogels, which indicate that adsorption occurs on both the interior and exterior surfaces. Quantitative EDS analysis results showed that the Cu loading in the WBH and MWH samples was about 1.8 wt%, in good agreement with the ICP-OES measurements (i.e., 1.85 ± 0.21 and 1.89 ± 0.17 wt% for WBH and MWH, respectively). The FTIR and XRD results of the Cu(II)-loaded MWH and WBH samples are presented in Fig. 6e and f. From the spectra, the FTIR spectra are quite similar for WBH or MWH before and after Cu(II) adsorption. The analysis on FTIR spectra shifting was done to further investigate the alteration of spectra caused by Cu(II) adsorption; that is by calculating the difference in wavenumber (δ) before and after adsorption. The highest δ was observed for the peak corresponding to O–H stretching and bending, as shown in Table 3 (the data were highlighted in bold font). Therefore, Cu(II) adsorption on the WBH and MWH affected the

12chemical bonds with O atoms; thus, it is reasonable to assume that the O atoms

play a significant role

29as the main adsorption sites for Cu(II) binding on the hydrogel surface

. 3.4.2.

8 Effect of pH on the Cu(II) removal efficiency

27 The pH at the point of zero charges (pHPZC) of the

sorbent material is crucial to its performance in removing adsorbate species (ions or molecules) under certain pH. A general consensus is that the surface of the sorbent is positively charged and thus can interact with negatively charged species at solution pHs lower than pHPZC, and vice versa [54]. The zeta potential vs. pH curve for WBH and MWH samples is depicted in Fig. 7a, demonstrating that both hydrogels exhibited pHPZC of about 6.7. Fig. 7b illustrates the

8 effect of solution pH on the removal efficiency of Cu(II) ions by the hydrogel sorbents. The

results indicate that the removal efficiency

33 increases with increasing solution pH and reaches a maximum at pH ~7

. At acidic pHs (pH < pHPZC), both the WBH and MWH surfaces bear a net positive charge and thus generate repulsive force toward Cu(II) ions. As the solution pH increases toward neutrality, the hydrogel surface carries a more negative charge from the deprotonated carboxyl groups, facilitating the uptake of metal ions through attractive electrostatic interactions. Meanwhile, the observed slight decrease of removal efficiency in an alkaline environment could be attributed to higher numbers of hydroxide anions that disrupt the interaction between the hydrogel surface and Cu(II) ions. 3.4.3. Effect of the initial concentration
Adsorbate concentration plays an important role in the adsorption process since it is the driving force affecting

7 the adsorption performance of an adsorbent. As shown in Fig. 7c, the equilibrium adsorption capacity (Q_e)

) of the sorbents increased with a higher initial concentration of Cu(II) ions, which can be attributed to the more significant interaction between the active sites of the sorbent and adsorbate molecules. In this regard, the high adsorbate concentration can create a concentration gradient that enhances the driving force of the adsorbate molecules. Summary of fitted kinetic parameters of P10, P20, Elovich, and IPD models for Cu(II) adsorption using WBH and MWH. Model and parameters Unit Value \pm SDa WBH MWH P10 Q1e mg/g k1 1/min R2 (Adj.) SSE P20 Q2e

9 mg/g k2 g/mg·min R2 (Adj.) SSE Elovich α mg/g min β g/mg RE R2

(Adj.) SSE IPD Ci,1

21 mg/g kIPD, 1 mg/g·min 0.5

R2 (Adj.) SSE Ci,

212 mg/g kIPD, 2 mg/g·min^{0.5}

R2 (Adj.) SSE Ci,3

21mg/g kIPD, 3 mg/g·min^{0.5}

R2 (Adj.) SSE 108.787 ± 2.894 0.019 ± 0.002 0.967 6.772 124.540 ± 3.011 0.028 ± 0.002 0.986 4.364 0.009 ± 0.001 0.040 ± 0.005 0.221 0.980 5.305 0.947 ± 0.019 9.005 ± 0.385 0.995 1.945 43.353 ± 6.452 3.837 ± 0.473 0.975 5.431 114.024 ± 0.000 ~0 1.000 0.000 116.395 ± 2.334 0.022 ± 0.002 0.976 5.812 128.407 ± 2.181 0.031 ± 0.003 0.990 3.718 0.031 ± 0.001 0.046 ± 0.005 0.184 0.975 5.978 1.125 ± 0.738 11.255 ± 0.865 0.977 5.238 70.936 ± 2.669 2.870 ± 0.199 0.981 1.500 119.111 ± 0.000 ~0 1.000 0.000 a SD = standard deviation. towards the adsorption sites. The concentration gradient force triggers the movement of the adsorbate in the bulk solution, which has a higher adsorbate concentration, toward the adsorbent [55,56]. However, at further increased adsorbate concentration, the %Cu removal began to decrease at high adsorbate concentrations (i.e., > 200 mg/L), as shown in Fig. 7d. This phenomenon occurs since there are more adsorbate molecules at higher concentrations but a similar number of active adsorption sites; thus, the adsorption sites tend to be saturated faster, and their adsorptivity decreases [57]. 3.5. Adsorption kinetics

2A kinetic adsorption study was conducted to investigate the adsorption rate and the

mechanism controlling at the given specific adsorption time. The adsorption kinetic profiles of WBH and MWH toward Cu(II) ions are displayed

4in Fig. 8. As can be seen in the figure, the uptake of

Cu(II) ions by the hydrogel samples proceeds rapidly within the first hour, after which it begins to slow as the system approaches equilibrium. The rapid adsorption at the initial stage can be ascribed to the abundant availability of adsorption sites on the hydrogel surface, which still possesses a high affinity toward the adsorbate ions. Meanwhile, the slow adsorption rate in the second step likely involves the diffusion of Cu(II) ions to the porous interior of the hydrogels [58]. Several

26kinetic models, namely pseudo-first-order (P1O) [59], pseudo-second-order (P2O) [60], Elovich [61], and intraparticle

diffusion (IPD) [62] models were employed to describe the sorption kinetics of Cu(II) by the hydrogel sorbents. The P1O model has a mathematical expression as follows: $Q_t = Q_1 e^{-k_1 t}$ (4)

17where Q_t and $Q_1 e^{-k_1 t}$ represent the amount of Cu(II) adsorbed per unit mass of adsorbent at time t and at equilibrium (mg/g), respectively, and k_1 is the P1O adsorption rate

constant (min^{-1}). The P2O model has a mathematical form as follows: $Q_t = Q_2 e^{-k_2 t} + Q_1 (1 - e^{-k_1 t})$ (5) where Q_2 represents the

32 amount of Cu(II) adsorbed per unit mass of adsorbent at equilibrium (mg/g), and k_2 is the

P2O rate constant (g/mg min^{-1}). The Elovich model has the following mathematical expression: $Q_t = \ln(1 + \alpha\beta t) / \beta$ (6) $RE = 1 - Q_{ref} / Q_{eq}$ (7) where α and β are empirical constants related to the adsorption ($\text{mg g}^{-1} \text{min}^{-1}$) and desorption (g mg^{-1}) rate constants, respectively. Q_{ref}

19 is the highest amount of Cu(II) adsorbed based on the experimental data (mg/g). The

parameter RE corresponds to

36 the approaching equilibrium parameter of Elovich equation

, which classifies an adsorption system into four zones as follows:

9 slow rising ($RE > 0.3$), mild rising ($0.1 < RE < 0.3$), fast rising ($0.02 < RE < 0.1$), and instant approaching equilibrium ($RE < 0.02$)

[63]. Finally, the IPD model can be expressed as follows: $Q_t = \sum_{i=1}^n k_{IPD,i} t^{0.5} + C_i$ (8) where k_{IPD} is the rate constant corresponding to a specific segment n (with $n = 1, 2, \text{ or } 3$) and C_i is an arbitrary constant related to the boundary layer effect [57,64]. All the kinetic parameters above were obtained by a nonlinear least-squares method using SigmaPlot 12 software package (Systat Software, Inc.) and the corresponding parameter values obtained upon fitting are reported in Table 4. As shown in Fig. 8, the P2O model gave a better agreement with experimental data than the P1O model, as indicated by lower sum-of-squared-error (SSE) values and the adjusted correlation coefficient (R^2 (Adj.)) close to unity. The fit parameters Q_2 and k_2 of the P2O model indicate that both the WBH and MWH have comparable adsorption performance toward Cu(II) ions in terms of the equilibrium adsorption capacity and removal rate constant. Moreover, the better correlation of kinetic data with P2O model suggests that the adsorption process by the hydrogels is limited by multistep diffusions [65], as discussed in more detail below. The Elovich model also provides good fits to the sorption kinetics curves with slightly lower R^2 values than the P2O model. From the analysis of RE , it can be implied that both Cu(II)-WBH ($RE = 0.22$) and Cu(II)-MWH ($RE = 0.18$) adsorption systems exhibited a mildly rising kinetic behavior, which is consistent with the experimental trend showing a fast uptake of metal ions during the initial stage (within 60 min) and followed by a slower second sorption step until the system reached equilibrium after 5 h. A multi-linear IPD model involving three segments demonstrates a good correlation with the experimental data (Fig. 8d). For WBH and MWH systems, the first segment (at $t = 0 - 7.75 \text{ min}$ or $t = 0 - 60 \text{ min}$) refers to the surface adsorption which indicates by higher rate compared to the next segment; i.e., $k_{IPD,1} > k_{IPD,2} > k_{IPD,3}$. The second segment occurs at $t = 7.75 - 17.32 \text{ min}$ ($t = 60 - 300 \text{ min}$); the segment refers to a gradual adsorption step that is controlled by intra-particle diffusion. The third segment at $t > 17.32 \text{ min}$ ($t > 300 \text{ min}$) refers to the equilibrium step in which the solute immigrates slowly to micropores in the inner matrix of the adsorbent, thus causing a slow (nearly zero) adsorption rate.

11 A similar phenomenon was reported in other studies related to adsorption

kinetics [58,64,66–68]. The rapid adsorption rate at the first segment occurs since the adsorbent has high vacant sites initially, and the solute concentration gradient in bulk and on the adsorbent surface is very high. As Fig. 9. Isotherm adsorption study of Cu(II) toward WBH and MWH at adsorption time = 8 h, pH = 7, temperature = 30 °C, adsorbent dosage = 0.2 g. The data were fitted using Langmuir, Freundlich, Sips, RP, DR, Temkin model. the adsorption proceeds, the vacant adsorbent sites occupy a certain number of solute molecules and create an interface between the solution and solute. Hereinafter, the adsorption of the remainder solutes is slowing down due to the higher energy barrier near the interface. Furthermore, a lower rate at higher segments indicates that the boundary layer limits the Cu(II) adsorption onto WBH or MWH.

3.6. Adsorption isotherms The evaluation of the adsorption isotherm was performed to give insights toward adsorption behavior in the investigated system. The isotherm study was conducted as a function of initial Cu(II) concentration from 5 to 500 mg/L. As shown in Fig. 9, WBH and MWH exhibited similar adsorption performance. The rapid increase in the Q_e was observed at Cu concentration < 100 mg/L, and the value of Q_e was nearly constant afterward, which indicates the saturation of the adsorbent material. The equilibrium

8 adsorption data were interpreted by several empirical isotherm models, namely Langmuir [69], Freundlich

[70], Sips [71], Redlich-Peterson (RP) [72], Dubinin-Radushkevich (DR) [73], and Temkin [74]. The classical Langmuir and Freundlich isotherm models have the mathematical forms expressed in Eqs. (9) and (10), respectively [75]. $Q_e = Q_{L,max} \frac{K_L C_e}{1 + K_L C_e}$ (9) $Q_e = K_F C_e^{1/n}$ (10) where $Q_{L,max}$ is the theoretical maximum (or monolayer) sorption capacity (mg/g), K_L is the Langmuir adsorption constant (L/mg), K_F is the Freundlich constant related to adsorption affinity (mg/g)(mg/L)⁻ⁿ, and Fitting parameters of isotherm adsorption of Cu(II) by WBH and MWH. Model and Unit Value ± SD a parameters WBH MWH Langmuir $Q_{L,max}$ KL RLb R2 (Adj.) SSE Freundlich KF nFc R2 (Adj.) SSE Sips QS aSd spd R2 (Adj.) SSE Redlich-Peterson KRP mg/g L/mg (mg/g)(mg/L)⁻ⁿ (mg/g) (L/mg) (L/g) aRP (L/mg) β_e aRPCe β_e R2 (Adj.) SSE Dubinin-Randushkevich QD (mg/g) B (mol²/kJ²) Ea (kJ/mol) R2 (Adj.) SSE Temkin BT (J/mol) KT (L/g) R2 (Adj.) SSE 261.136 ± 39.353 0.009 ± 0.003 0.182 0.943 17.681 7.611 ± 4.214 1.736 0.106 ± 0.881 25.607 173.586 ± 4.869 0.218 0.028 ± 0.946 ± 0.027 0.992 6.535 1.508 ± 0.161 0.00001 ± 0.00001 2.198 ± 0.495 0.302 0.979 10.689 214.846 ± 10.392 0.005 ± 0.001 10.206 0.978 10.933 54.234 ± 6.155 0.147 ± 0.041 0.885 25.241 235.068 ± 26.609 0.011 ± 0.003 0.153 0.955 15.273 8.961 ± 4.479 1.852 0.096 ± 0.887 24.098 167.795 ± 3.644 0.159 0.012 ± 0.929 ± 0.109 0.995 5.034 1.779 ± 0.231 0.00001 ± 0.00001 1.657 ± 0.331 0.388 0.979 10.373 198.019 ± 6.354 0.007 ± 0.0007 8.392 0.988 7.975 56.185 ± 5.405 0.159 ± 0.039 0.915 20.979 a SD standard deviation. = b The process is favorable when 0 < RL < 1, unfavorable when RL >> 1 [76–78]. c An nF value between 1 and 10 indicates the favorable process [83]. d The model reduces to Langmuir when sp value is equal to 1, and to Freundlich when aS approaches 0 [84,85]. e The

7 model reduces to Langmuir as the β equal to 1, and to Freundlich when

aRPCe β is much bigger than 1 [84]. nF is the factor describing the

16 favorability of the sorption process. The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless

equilibrium parameter (RL) [76], defined as follows: $RL = \frac{1}{1 + K_L C_0}$ (11) The values of RL indicate the Langmuir-type adsorption isotherm to be either unfavorable ($RL > 1$), linear ($RL = 1$), favorable ($0 < RL < 1$), $> = <<$ or irreversible ($RL = 0$). The DR model has a mathematical form as follows: $Q_e = Q_D \exp\left(-\frac{B}{RT} \ln\left(1 + \frac{C_e}{2}\right)\right)$ (12) $E_a = \sqrt{1 + \frac{2B}{RT}}$ (13) Table 6 Comparison of adsorption capacities and Kd values of WBH and MWH with other cellulose-based materials and composites toward Cu(II) ions. Adsorbent pH Qm (mg/g) Kd (mL/g) Fitting model Ref. Kinetics Isotherm WBH MWH Cellulose hydrogel Cellulose/ gelatin hydrogel Straw-derived hydrogela GO/cellulose hydrogelb Chitosan/ cellulose hydrogel beads MDSDc Collagen/ cellulose hydrogel beads PEI-RCSAd WP/PAM hydrogela 7 114.0 7 119.1 4.7 28.3 4.7 52.3 n. 90.3 a. 5.3 94.3 6.7 53.2 6 6 4.3 29.8 5.5 3–6 120.0 139.5 1325.6 1472.2 98 187.4 172.4 494.5 N/A N/A 110.0 P2O P2O n.a. n.a. P2O P2O n.a. n.a. n.a. 1500 P2O 5.9 × 10⁴ P2O Langmuir This work Langmuir This work Freundlich [86] Freundlich [86] Freundlich [87] Freundlich [88] Langmuir [89] Langmuir Langmuir [90] [91] Langmuir Langmuir [92] [93] a Wheat straw containing cellulose, hemicellulose, and lignin was used as the raw material. b GO graphene oxide. = c MDSD refers to modified sawdust cellulose using esterification. d Polyethyleneimine-functionalized crosslinked cellulose/sodium alginate. e WP/PAM waste paper/acrylamide double-network hydrogel. = where QD is the DR adsorption capacity, B

18 is the mean free energy of adsorption

(mol²/kJ²),

18 R is the gas constant (8.314 J/mol K), and Ea is the adsorption energy (kJ/mol). The

three-parameter Sips and RP isotherm models have the mathematical forms expressed in Eqs. (14) and (15), respectively: $Q_e = Q_S \left(1 + \frac{a S C_e^{1/sp}}{1 + a S C_e^{1/sp}}\right)^{sp}$ (14) $Q_e = \frac{1}{1 + K_R a P R C P e C \beta e}$ (15) where, for the

7 Sips model, QS is Sips adsorption capacity, aS is a constant related to adsorption energy, and sp is the Sips model exponent. For the

RP model, KRP (L/g) and aRP (L/mg) is the RP constant, and β is the RP model exponent. Finally, the Temkin model has the mathematical form as follows: $Q_e = \frac{RT}{B} \ln(KT C_e)$ (16)

31 where KT is a binding constant (L/g), and BT is a constant related to the heat of adsorption (J/mol). The

calculated parameters of the isotherm model

1 obtained from the nonlinear least-square analysis are presented in Table 5. As

shown in Fig. 9, the Langmuir model can describe the experimental data very well, which is signified by higher correlation coefficients (i.e., $R^2 \sim 1$ and = low SSE) than the Freundlich model. Moreover, the RL values of the Langmuir model fall within $0 < RL < 1$ for the adsorption systems, $<<$ indicating that the adsorption of Cu(II) ions onto WBH and MWH sorbents is favorable [76–79]. The nF of the Freundlich model shows a value between 1 and 10 for both systems, indicating the favorability of the process; this parameter is in good agreement with the RL value. The three parameters models of Sips and RP was applied to assess the

systems tendencies toward Langmuir or Freundlich models. The Sips model has better applicability to represent the adsorption data than the RP model, as indicated by the higher correlation coefficients. Furthermore, the sp value of the Sips model is close to 1, indicating its inclination to the Langmuir model. The adsorption mechanism and energy can be evaluated from DR and Temkin model. The E_a value of WBH and MWH systems is larger than 8 kJ/mol; thus, it can be proposed that the chemisorption is dominant in the investigated adsorption systems [80–82]. The positive BT value of the Temkin model suggests that the Cu (II) adsorption by WBH or MWH was exothermic [80], and therefore, the adsorption would be more favorable at a lower temperature. 3.7. Performance comparison of the adsorbent materials Table 6 summarizes the adsorption performances of various cellulose-based materials and composites

26**for Cu(II) removal from aqueous solutions** in terms of **the**

maximum sorption capacity (Q_m) and K_d metrics. It can be seen that the as-synthesized WBH and MWH materials exhibit Q_m values that are superior to most of the reported cellulose-based adsorbents in the literature, such as GO/cellulose, chitosan/cellulose, and collagen/cellulose composites. The excellent performance of WBH and MWH in removing Cu(II) ions is also reflected from their K_d values. It was found that the K_d values of WBH and MWH for Cu(II) reach 1325.6 and 1472.2 mL/g, respectively, which are considerably larger than the K_d values of other cellulose-based hydrogel sorbents (the consensus is that an excellent heavy metal adsorbent exhibits K_d value higher than 104 mL/g [20]). Regarding the kinetic fitting model, it can be implied that most of the adsorption systems reported in the literature obey the P2O model, thus suggesting that the uptake of Cu (II) ions by cellulose-based materials primarily occurs via chemisorption. Meanwhile, some prior studies showed better data

27**fit to the Freundlich and** others with **Langmuir isotherm models** for **the**

sorption equilibrium. 4. Conclusions In summary, we have demonstrated the preparation of ECH cross-linked cellulose hydrogels by using conventional WB heating at 60 °C and MW irradiation processes. Both heat activation methods were shown to produce hydrogels with similar physicochemical characteristics in terms of the surface and porous morphology, chemical composition, thermal stability, and equilibrium swelling ratio. However, the use of MW irradiation to facilitate crosslinking reaction between free cellulose fibrils and ECH molecules offers a more economical use of energy and time compared to the conventional WB heating. Notably, the hydrogel formation was completed within 3 min under MW irradiation at 400 W, where a longer crosslinking reaction time (20 min) was needed for WB heating. The life-cycle cost analysis under an industrial scale scenario study revealed that the production cost of the hydrogel is similar by using conventional WB or MW heating procedures. Batch adsorption results of WBH and MWH toward Cu(II) ions demonstrated that the maximum removal efficiency occurred at pH 7 and kinetic equilibrium was reached after 60 min. Adsorption kinetics curves of Cu (II) ions by WBH and MWH exhibited a mildly rising behavior (zone II)

36**based on the approaching equilibrium parameter (RE) of Elovich**

equation and were

4**best fit to the P2O model, thus suggesting the**

chemisorption nature of the adsorption. Meanwhile, the equilibrium adsorption data was best interpreted by the Langmuir model, indicating monolayer adsorption on the hydrogel sorbent with the theoretical maximum

capacity (QL,max) of 261.1 and 235.1 mg/g for WBH and MWH, respectively. Overall, this work demonstrates that MW irradiation technique offers great potential for rapid, low-cost, and energy-efficient preparation of cellulose hydrogels. However, further studies are needed to investigate the effects of MW irradiation power and duty cycles on the degree of crosslinking, which subsequently affects the mechanical properties and porous structure of the resultant hydrogel materials. In the latter context, such detailed experimental studies would provide vital information for developing high-performance porous hydrogel-based adsorbents with fast kinetics and high uptake capacity for toxic metal ion capture from water and wastewater.

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. Alfin Kurniawan:

2Formal analysis, Writing – review & editing, Resources, Supervision

. Maria Yuliana: Writing – review & editing.

2Chang-Wei Hsieh: Project administration, Writing original – draft. Alchris Woo Go: Formal analysis, Validation. Kuan-Chen Cheng: Writing review editing

2Felycia Edi Soetaredjo: Methodology, – & Resources. Suryadi Ismadji: Conceptualization, Supervision

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