

Hydrogels from dextran/carboxymethyl cellulose exhibiting high post-drying swelling ratios and recovery

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Abstract: Hydrogels were prepared from enzymatically synthesized (1→6)- α -D-glucan (dextran) and carboxymethyl cellulose (CMC) by crosslinking with ethylene glycol diglycidyl ether. The resulting dextran/CMC hydrogel was transparent, highly swellable, and self-standing. Analyses revealed that the swelling ratio of the hydrogels increased as the CMC content increased. Further, the CMC hydrogel was hard but brittle, with a relatively high elastic modulus (15.8 kPa) and low fracture strain (10.5%). With increasing dextran content, the dextran/CMC hydrogels became softer and more flexible, the elastic modulus decreased, and the fracture strain increased. The oven-dried samples of the dextran/CMC hydrogel exhibited the ability to restore their shape and size when immersed in deionized water. The adsorption of heavy metal Cu^{2+} ions and methylene blue dye on the dextran/CMC hydrogel was well described by pseudo-second-order kinetics and Freundlich isotherm models. The reusability test showed that the dextran/CMC hydrogel is a potential adsorbent that can be reused multiple times.

Keywords: adsorbent, carboxymethylcellulose, compression test, dextran, ethylene glycol diglycidyl ether, hydrogel

Introduction

With rapid industrialization, a large number of toxic pollutants have been released into the environment. Wastewater containing heavy metal ions and organic pollutants flows directly or indirectly into rivers, lakes, and oceans, thereby seriously affecting various living organisms and the environment, as well as posing a threat to human health (Huang et al. 2013; Qi et al. 2018). To address these problems, various technologies and approaches, such as membrane filtration, ion exchange, electrochemical treatment, flotation, and adsorption, have been adopted to remove specific pollutants from wastewater (Bessbousse et al. 2008; Dabrowski et al. 2004; Mohtashami and Shang 2019). Adsorption is the most feasible method because of its many advantages, such as eco-friendliness, simplicity, and high efficiency, in removing contaminants (Karaer and Kaya 2016; Luo et al. 2019). Therefore, the development of novel materials with high adsorption performance is currently in demand.

Hydrogels are three-dimensionally crosslinked polymer materials that absorb and retain large amounts of water and are highly flexible. Synthetic polymers such as hydrophilic polyacrylic acid are commonly used as superabsorbent hydrogels (Ahmed 2015; Capanema et al. 2018). However, from an environmental point of view, the use of polysaccharides such as cellulose as a raw material is more environmentally friendly because cellulose is a photosynthetic product and is carbon-neutral (Hong et al. 2018; Panchan et al. 2018). Moreover, various derivatives have been developed to impart and/or modify cellulose functionality. One of the major ether derivatives of cellulose is CMC, which is generally produced from the reaction of cellulose with chloroacetic acid under alkaline conditions. CMC has a heterogeneous structure, in which some hydroxyl groups of cellulose are replaced with carboxymethyl groups. Therefore, CMC is water-soluble and can be used as a viscosity modifier, emulsion stabilizer, and water retention agent in various products, such as detergents, cosmetics, food, and paint (Zennifer et al. 2021; Zhu et al. 2021). CMC hydrogels prepared by physical or chemical crosslinking exhibit excellent swellability and can adsorb a wide range of heavy metals and dyes. Several studies have reported the applications of CMC hydrogels as adsorbents for removing heavy metal ions and dyes (Dahlan et al. 2017; Mittal et al. 2021).

Dextran is a water-soluble polysaccharide consisting of α -(1 $\rightarrow$ 6)-D-linked glucose as a backbone with branches extending mainly from the α -(1 $\rightarrow$ 3) linkages. Dextran is commonly synthesized as an exopolysaccharide by several mesophilic and thermophilic bacterial genera of *Leuconostoc*, *Streptococcus*, *Gluconobacter*, and *Lactobacillus* (Díaz-Montes 2021). However, dextran production is inefficient because a lot of energy is consumed in the metabolism of the

bacteria. Some glucosyltransferase (Gtf) enzymes, also known as glucansucrases of the glycoside hydrolase family 70 (GH70), are known to synthesize dextran from plant-derived sucrose. The degree of branching and molecular weight of the synthesized dextran vary greatly depending on the enzyme and synthetic conditions; however, the recombinant GtfK enzyme, which is one of the Gtf enzymes obtained from *Streptococcus salivarius*, can synthesize highly pure dextran with high molecular weight and without branching (He et al. 2020; Simpson et al. 1995). Especially, the yield of dextran synthesis from sucrose by GtfK is very high at 80% (He et al. 2020). In a previous report, we prepared a transparent and highly swellable hydrogel from GtfK-synthesized dextran cross-linked with ethylene glycol diglycidyl ether (EGDE) and found that it was soft and flexible. Once the dextran hydrogel was dried and immersed in water, its shape, size, and appearance returned to their original states, indicating the feasibility of this hydrogel for use as a highly absorbent material (He et al. 2020). However, the dextran hydrogel only has a hydroxyl group as a functional group in its molecular chain and is not suitable for absorbing contaminants such as heavy metals and dyes.

Therefore, in this study, we prepare a highly swellable hydrogel as a versatile adsorbent material with soft and flexible properties by mixing CMC with branchless dextran.

Experimental

Preparation of dextran/CMC hydrogel

Branchless dextran (molecular weight $M_w = 2.3 \times 10^5$ g/mol, dispersity $D_M = 2.6$) was synthesized from sucrose using a recombinant GtfK enzyme obtained from *S. salivarius* (ATCC 25975) according to the previously reported method (He et al., 2020). Sodium CMC (Aldrich, average $M_w = 2.5 \times 10^5$ g/mol, degree of substitution = 0.7) was used without further purification. Dextran and sodium CMC, with a total mass of 0.5 g, were dissolved in 10 mL of 1 N NaOH aqueous solution at various ratios. EGDE (1.0 g) was added dropwise to the solution under gentle stirring (**Fig. 1**). The mixture (0.8 mL) was injected into a cylindrical plastic mold of 1.0 cm in diameter and 1.0 cm in height, and left to stand in a desiccator (relative humidity (RH) = 100%) at 23 °C. After 24 h, the crosslinked hydrogel was carefully removed from the mold and washed several times with deionized water until the pH became neutral. A portion of the washed hydrogel was stored in the wet state in a refrigerator, whereas the rest of the washed hydrogel was oven-dried at 60 °C. All the prepared dextran/CMC hydrogels are listed in **Table 1**.

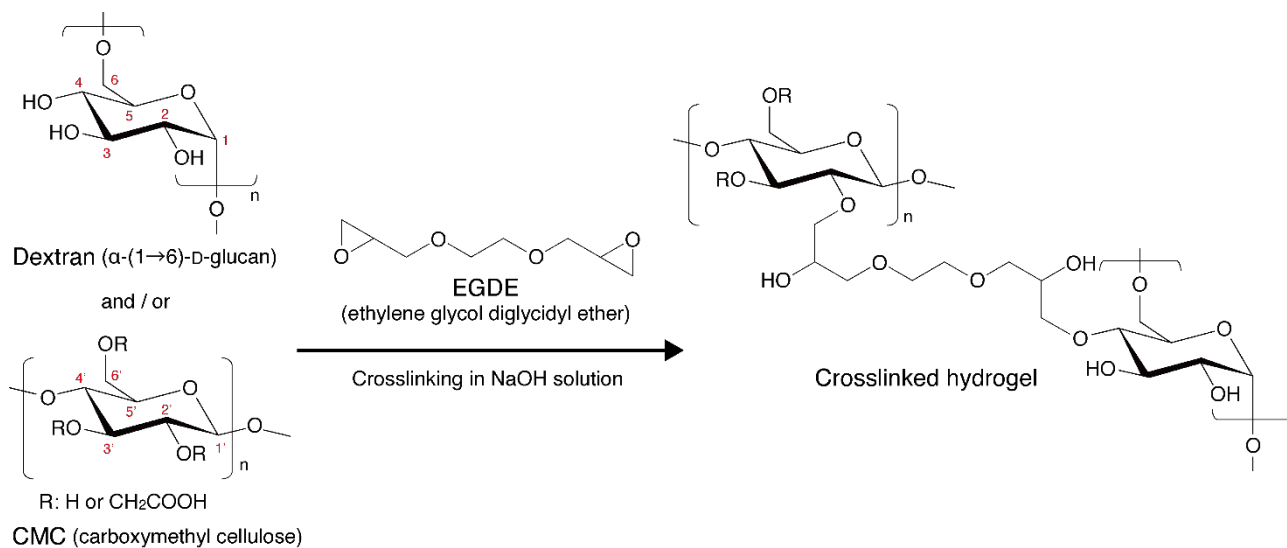


Fig. 1 Crosslinking reaction of dextran and/or CMC with EGDE.

Characterization

Fourier-transform infrared spectroscopy (FTIR) was performed using the KBr method (IRPrestige-21, Shimadzu Corporation, Japan). The FTIR measurements were performed in absorbance mode in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. Solid-state cross-polarization magic angle spinning (CP/MAS) ¹³C nuclear magnetic resonance (NMR) spectra were obtained using a 400 MHz solid-state NMR spectrometer (VARIAN, USA) with a 4 mm double-resonance probe. The measurement parameters were as follows—spinning speed rate: 15 kHz; plus delay time: 5 s; number of scans: 2048.

Rheological measurements of the swollen hydrogels were performed using a stress-controlled rheometer (MCR302, AntonPaar GmbH, Austria) with a parallel plate jig (diameter of 25 mm) at 23 °C. Strain sweep measurements were conducted at a strain of 0.1–100% and at a frequency of 1 Hz, and the linear viscoelastic region was obtained with 0.1 % strain. Frequency sweep measurements with a constant strain 0.1% were subsequently performed at an angular frequency ω of 0.1–100 rad s⁻¹.

Hydrogels were exchanged with solvents (ethanol $\rightarrow$ t-butyl alcohol). Freeze-dried gels fractured in liquid nitrogen were coated with metallic osmium. The morphology of the fractured surface was observed using a Scanning Electron Microscope (SEM) (Hitachi S-4800, Japan).

Compression tests of the hydrogels were conducted with constant temperature and humidity (23 °C, RH = 50%) using a testing machine (EZ-Test, Shimadzu Corporation, Japan) equipped with a 100-N load cell. Cylindrical hydrogels were compressed at a speed of 1 mm/min using a measuring plate, and five samples of each hydrogel were tested for the compression analysis. The elastic modulus was determined from the linear region of the stress–strain curve.

Measurement of swelling characteristics

pH and salt sensitivity

To investigate the swelling behavior, the hydrogels were immersed in deionized water and a series of solutions with ascending pH (adjusted with HCl and NaOH solutions) for three days to reach equilibrium. The hydrogels were then immersed in 0.1–1.0 wt% salt solutions (KCl, CaCl₂, and FeCl₃) for three days. The weights of the hydrogels were measured after removing the excess solution from the surface. The hydrogels were then dried at 105 °C for 24 h, and the equilibrium swelling ratio (S_r) was determined as follows:

$$S_r (\%) = \frac{M_e - M_d}{M_d} \quad (1)$$

where M_e and M_d are the weights of the hydrogel after reaching equilibrium (by immersion in the solution for three days) and the dried hydrogel, respectively.

Water-swelling kinetics and recovery ratio

The water-swelling kinetics and recovery of the oven-dried gels were determined by immersing the dried gels in deionized water at room temperature. The hydrogel was then removed from the deionized water at specific times and weighed after wiping the excess solution from the surface. The first 60% of the water uptake (W_u) was fitted using the Peppas kinetic equation (Khare and Peppas, 1995):

$$W_u (\%) = \frac{M_t - M_d}{M_r - M_d} \times 100$$

$$= kt^n \quad (2)$$

where M_t is the weight of the re-swollen hydrogel at time t , M_d is the weight of dried hydrogel before re-swollen, M_r is the weight of re-swollen hydrogel after equilibrium (by immersion in deionized water for three days), k is the diffusion constant, and n is the diffusion exponent. The recovery ratio (R) of the hydrogels was calculated as follows:

$$R (\%) = \frac{M_r}{M_e} \times 100 \quad (3)$$

where M_e and M_r are the same as those stated in Eqs. (1) and (2), respectively.

Adsorption measurement

The adsorption of a heavy metal ion (Cu^{2+}) and hydrophilic dye (MB) on the dextran/CMC hydrogel was examined using batch adsorption experiments. The dried gel samples (35 mg) were immersed in a series of Cu^{2+} (25 mL) and MB (35 mL) solutions of different concentrations at 25 °C for up to three days. After reaching adsorption equilibrium, the concentration of the supernatant was measured using a UV-vis spectrophotometer (UV-2450, Shimadzu Corporation, Japan) at the maximum absorption wavelengths of 810 nm and 664 nm for the Cu^{2+} and MB solutions, respectively.

The amount of dye and heavy metal ion adsorbed onto the dextran/CMC hydrogels (q_e , mg/g) is defined as follows:

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (4)$$

where C_0 and C_e are the initial and final concentrations (mg/L) of the MB and Cu^{2+} solutions, respectively, V is the volume, and m is the mass of the dried gel.

Adsorption kinetics

The adsorption kinetics were investigated using pseudo-first-order and pseudo-second-order kinetics models, defined by the following equations:

$$q_t = q_e \{1 - \exp(-k_1 t)\} \quad (5)$$

$$q_t = \frac{t q_e^2 k_2}{t k_2 q_e + 1} \quad (6)$$

where q_t and q_e are the adsorption amounts (mg/g) at time t and equilibrium ($t = 3$ d), respectively, whereas k_1 and k_2 are the rate constants from the pseudo-first-order and pseudo-second-order kinetics models, respectively.

Adsorption isotherms

The adsorption isotherms were investigated using the Langmuir and Freundlich models, defined by the following equations:

$$q_e = \frac{q_m K_L C_e}{K_L C_e + 1} \quad (7)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (8)$$

where q_m is the theoretical maximum adsorption capacity (mg/g), K_L is the Langmuir equilibrium constant, C_e is the equilibrium concentration (mg/L), K_F is the Freundlich equilibrium constant, and n is a heterogeneity factor.

Reusability of the dextran/CMC hydrogels

The reusability of the dextran/CMC hydrogel was examined by performing successive adsorption–desorption cycles. The dried dextran/CMC hydrogel (D1C1-1, 35 mg) was immersed in 25 mL and 35 mL of 50 mg/mL Cu^{2+} and MB solutions, respectively, at 25 °C, for three days, with stirring. The hydrogels with absorbed Cu^{2+} and MB were then treated with 0.1 M HCl solutions at 25 °C and washed with deionized water several times (Isobe et al. 2013; Mittal et al. 2021). The washed hydrogels were dried at 60 °C for 24 h and subjected to the next adsorption–desorption cycle.

Results and discussion

Characterization

The FTIR spectra of the dextran, CMC, and D1C1-1 hydrogels, together with those of native dextran and CMC, are shown in **Fig. 2a**. Common features of all the spectra are the OH stretching band at 3429 cm^{-1} , CH stretching band at 2927 cm^{-1} , and C–O–C stretching at 1159 cm^{-1} . Asymmetric COO^- bands appeared at 1606 cm^{-1} in the spectra of the CMC, CMC hydrogel, and D1C1-1 hydrogel (Kono et al. 2013). The peak at 2881 cm^{-1} , which is attributed to the CH_2 stretching band of the EGDE crosslinkers (He et al. 2020), became more prominent in the spectra of the hydrogels than in those of dextran and CMC.

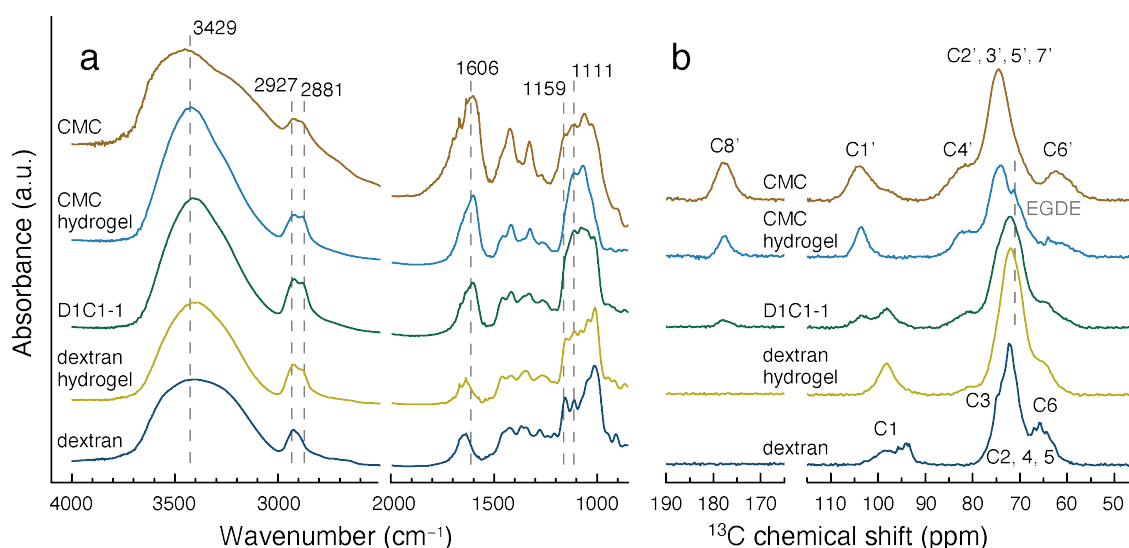


Fig. 2 (a) FTIR and (b) solid-state ^{13}C NMR spectra of the dextran, CMC, and D1C1-1 hydrogels compared with those of dextran and CMC.

Solid-state ^{13}C NMR spectra of the dextran, CMC, and D1C1-1 hydrogels, as well as those of dextran and CMC are shown in **Fig. 2b**. In the spectra of dextran and its hydrogel, C1 and C6 peaks appeared in the 100–90 ppm and 64–61 ppm regions, respectively. Additionally, the broad peak in the 75–66 ppm region overlapped with the C2, C3, C4, and C5 peaks (He et al. 2020). In the spectra of CMC and its hydrogel, the peaks appearing at 178, 104, and 83 ppm were assigned to the carbonyl carbon (C8'), C1', and C4', respectively; the peak at 74 ppm represents overlapping signals of C2', C3', C5', and the methylene carbon (C7'); the peak at 62 ppm is assigned to C6'. (Kono et al. 2013). The methylene carbons of EGDE appeared as a shoulder at 71 ppm in the spectrum of the CMC hydrogel (indicated by the dotted line in **Fig. 2b**) (He et al. 2020; Kono et al. 2013). However, in the spectrum of the dextran hydrogel, this peak overlapped with the broad peaks of C2, C3, and C5. The spectrum of D1C1-1 shows the combined features of the spectra of both dextran and CMC hydrogels. These results indicate that the D1C1-1 hydrogel was successfully synthesized from dextran and CMC by crosslinking with EGDE.

Physical characteristics of the dextran/CMC hydrogel

Dextran and CMC that were crosslinked with EGDE in molds of 1 cm diameter swelled 1.5- to 3-fold in diameter after washing and immersion in deionized water for three days. The shapes of the swollen hydrogels on a 1 cm square grid are shown in **Fig. 3a–b**. The hydrogels were clear and colorless. The D1C1-0.5 hydrogel greatly expanded into irregular shapes, whereas the other hydrogels maintained their original cylindrical shape and self-standing ability.

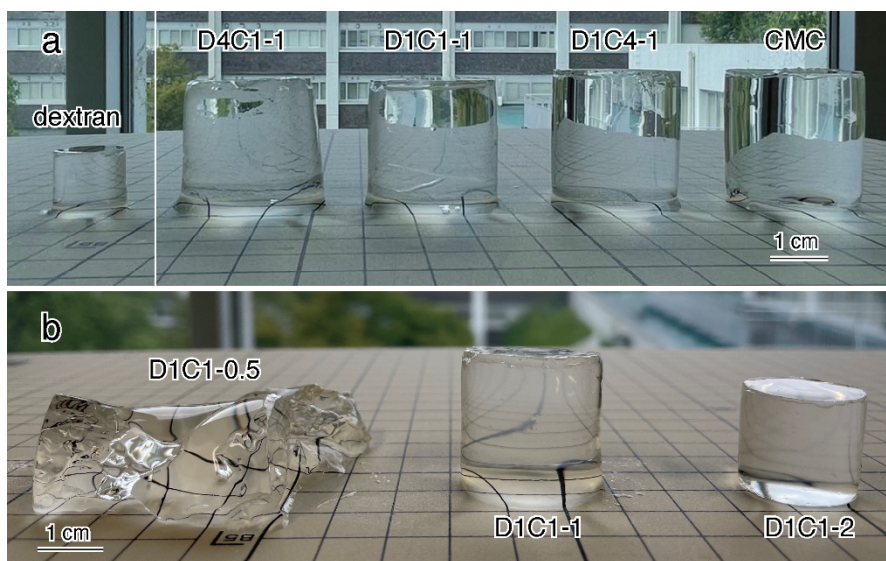


Fig. 3 Photographs of the hydrogels on a 1 cm square grid after washing and immersion in deionized water. (a) Dextran, dextran/CMC, and CMC hydrogels with 1 g EGDE dosage. (b) Dextran/CMC (D1C1) hydrogels with different EGDE dosages (0.5, 1, and 2 g).

The swelling ratios of the dextran/CMC hydrogels are summarized in **Table 1**. The swelling ratio of the dextran hydrogel was 3460%. As the ratio of CMC to dextran increased, the swelling ratio also increased (see the swelling ratios of D4C1-1, D1C1-1, and D1C4-1). At the 1:4 ratio of dextran to CMC, the swelling ratio reached 20 380% (D1C4-1), which is almost the same as that of the CMC hydrogel (21 600%). At the same dextran/CMC ratio of 1, the swelling ratio of the hydrogels gradually increased from 8280% to 52 890% as the crosslinker dosage decreased (D1C1-2, D1C1-1, and D1C1-0.5). The D1C1-0.5 hydrogel absorbed water more than 500 times its own weight, which is remarkable as a polysaccharide-based hydrogel.

Table 1 Amounts of CMC, dextran, and EGDE added in preparing dextran/CMC hydrogels, as well as the swelling ratio and mechanical properties of the hydrogels

Sample	Dextran (g)	CMC (g)	EGDE (g)	Swelling ratio (%)	Fracture stress (kPa)	Fracture strain (%)	Elastic modulus (kPa)
Dextran	0.5	0	1	3460	29.0 ± 6.0	75.9 ± 3.9	2.19 ± 0.3
D4C1-1	0.4	0.1	1	17 990	1.53 ± 0.5	29.4 ± 2.9	2.58 ± 0.2
D1C1-1	0.25	0.25	1	18 940	4.56 ± 3.2	24.3 ± 6.2	7.39 ± 1.6
D1C4-1	0.1	0.4	1	20 380	2.26 ± 0.5	14.3 ± 3.2	13.9 ± 1.7
D1C1-0.5	0.25	0.25	0.5	52 890	—	—	—
D1C1-2	0.25	0.25	2	8280	19.8 ± 3.2	21.2 ± 8.9	30.1 ± 3.1
CMC	0	0.5	1	21 600	1.37 ± 0.2	10.5 ± 2.9	15.8 ± 3.8

Compression tests were performed on the swollen hydrogels, and the stress–strain curves are shown in **Fig. 4**. The stress–strain curves of the hydrogels are typical of those from the compression of soft materials, in which the stress gradually increases in the region where the strain is small and increases significantly when the strain is large. As the

amount of CMC in the hydrogels increased, the slope of the low-strain region increased, and fracture occurred at a low strain. Further, when the crosslinker dosage was doubled (D1C1-2), the initial slope of the stress–strain curve and the fracture stress increased.

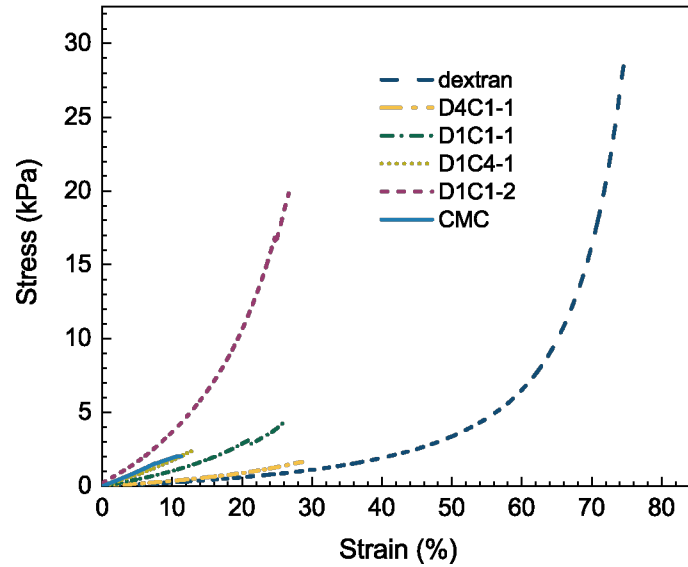


Fig. 4 Stress–strain curves from compression test of the dextran, dextran/CMC, and CMC hydrogels.

The elastic modulus, fracture stress, and fracture strain values are listed in **Table 1**. The elastic moduli of the hydrogels increased when the CMC content was increased from 2.19 kPa (dextran hydrogel) to 15.8 kPa (CMC hydrogel). The fracture stress and strain values of the dextran hydrogel were 29.0 kPa and 75.9%, respectively, which are rather higher than those of the dextran/CMC and CMC hydrogels. When more than 20% CMC was present (D4C1-1, D1C1-1, and D1C4-1), the fracture stress values of the hydrogels were almost the same as that of the CMC hydrogel. In contrast, the fracture strain values decreased as the amount of CMC increased. When the ratio of dextran/CMC was the same and the crosslinker dosage was doubled (D1C1-2), the elastic modulus and fracture strength were significantly improved. These results show that as the dextran/CMC ratio decreased, the hydrogels became weaker and more brittle than the dextran hydrogel. However, when the crosslinker dosage was high, the dextran/CMC hydrogel became harder and stronger. The D1C1-1 hydrogel had the strongest structure among the dextran/CMC hydrogels; thus, it was selected for use in the subsequent experiments.

The dynamic viscoelastic measurements were performed on the swollen hydrogels, and storage moduli (G') and loss moduli (G'') are shown in **Fig. 5**. The storage moduli of dextran, D1C1-1, and CMC hydrogels were in the range of 100-200 Pa. In all samples, the storage moduli were greater than the loss moduli, and $\tan\delta$ was less than 1. Thus, it can be concluded that all the hydrogels maintained elastic state in the measured frequency range.

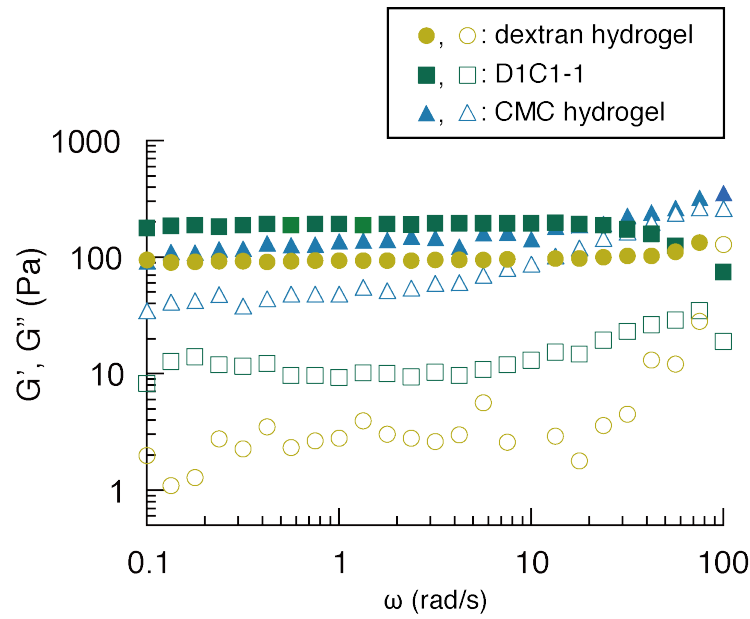


Fig. 5 Storage moduli (G' , filled symbols) and loss moduli (G'' , filled symbols) of the dextran, D1C1-1, and CMC hydrogels as a function of angular frequency (ω).

Freeze fracture surface of the dried dextran, D1C1-1, and CMC hydrogels were observed by SEM (**Fig. S1**). The dried dextran hydrogel had micropores almost uniform size (1.8-10.3 μm), while the dried D1C1-1 and CMC hydrogels had many micropores with a wide size distribution (1.2-25.9 μm). These voids were probably created during freezing.

Swelling behavior of the dextran/CMC hydrogel

The swelling ratios of the dextran, D1C1-1, and CMC hydrogels and the appearance of the D1C1-1 hydrogels under different pH conditions are shown in **Figs. 6a** and **6b**, respectively. The swelling ratio of the dextran hydrogel remained almost constant (approximately 4000%) in the pH range of 2–11, whereas those of D1C1-1 and CMC hydrogels exhibited pH sensitivity. The swelling ratios of the D1C1-1 and CMC hydrogels were higher in the pH range of 5–8, approximately

18 000% and 20 000%, respectively, but lower in the acidic and alkaline regions. This swelling behavior can be explained by the dissociation of the carboxyl groups and the effect of electrostatic repulsion. In the neutral region (pH 6–8), the carboxyl groups in the CMC molecules are present in the deprotonated form ($-\text{COO}^-$), enhancing the electrostatic repulsion between the carboxyl groups. As a result, more water could be absorbed by the hydrogel. In the alkaline region (pH > 9), excess Na^+ counterions shielded the $-\text{COO}^-$ anions, which suppressed anion–anion repulsion between the carboxyl groups, causing the hydrogel to shrink. In contrast, the carboxyl group ($-\text{COO}^-$) turns to the protonated form ($-\text{COOH}$) under acidic conditions and forms strong hydrogen bonds among the $-\text{COOH}$ groups, restricting the swelling of the hydrogel. At pH 2, the swelling ratios of the D1C1-1 and CMC hydrogels were the lowest (approximately 3800%), which was the same value as the dextran hydrogel. This result indicates that the carboxyl groups are completely protonated and there is no swelling of the hydrogels due to the electrostatic repulsion effect (Chang et al. 2011; Xu et al. 2015; Zhang et al. 2017).

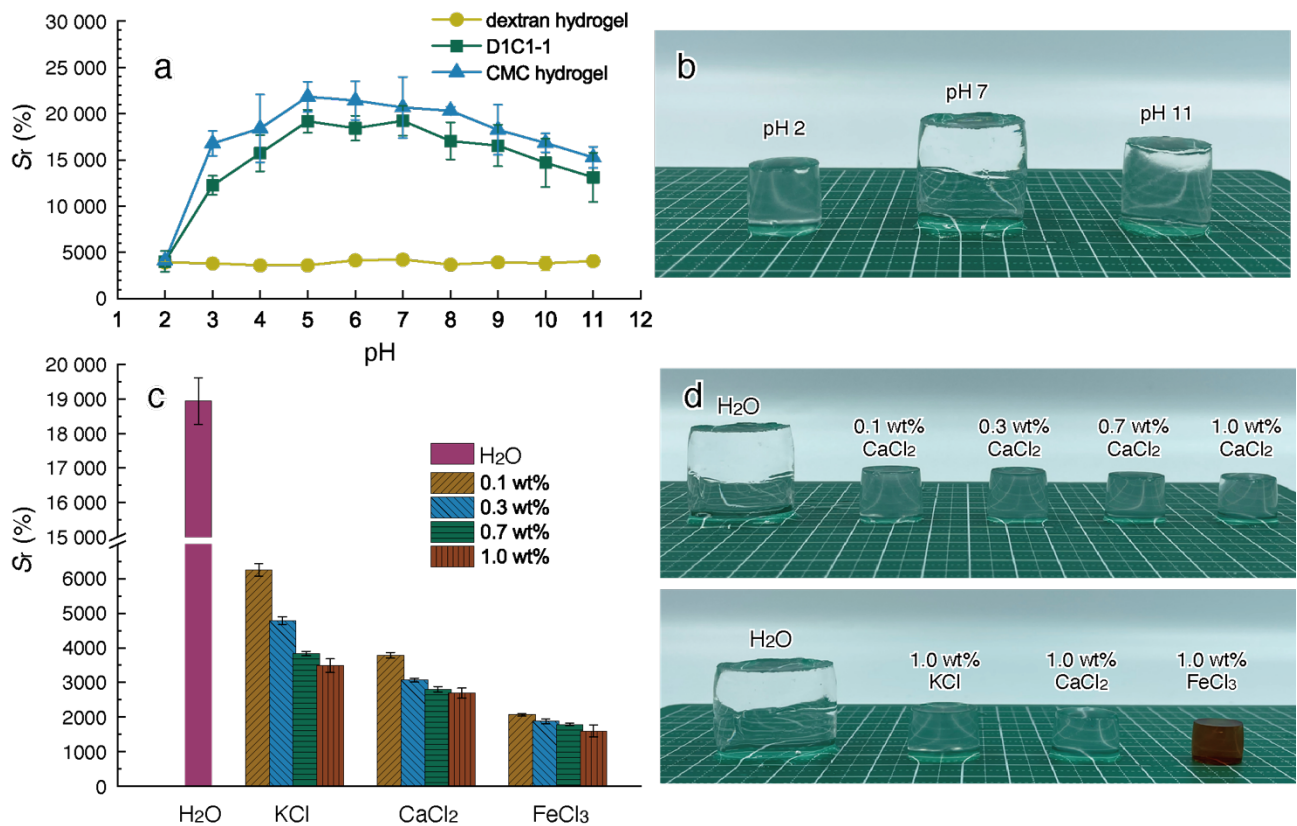


Fig. 6 (a) Swelling ratios of the dextran, D1C1-1, and CMC hydrogels in various pH solutions and (b) images of the swollen D1C1-1 hydrogel after immersion in solutions at pH 2, 7, and 11. (c) Swelling ratio of the D1C1-1 hydrogels in

deionized water and different concentrations of KCl, CaCl₂, and FeCl₃ salt solutions and (d) images of the swollen D1C1-1 hydrogel after immersion in deionized water and 1.0 wt% of KCl, CaCl₂, and FeCl₃ salt solutions.

The swelling ratio and images of the swollen D1C1-1 hydrogels in deionized water and in KCl, CaCl₂, and FeCl₃ solutions of different concentrations are presented in **Figs. 6c** and **6d**, respectively. The swelling ratio of the D1C1-1 hydrogels was smaller in salt solutions (2000–6000%) than in deionized water (18 940%), which indicates that the presence of K⁺, Ca²⁺, and Fe³⁺ cations in the solution caused a substantial decrease in the water absorbency of the D1C1-1 hydrogel. As the concentration of the salt solution increased, the swelling ratio of the D1C1-1 hydrogel decreased. For example, in CaCl₂ solutions, the swelling ratios of the hydrogels in 0.1 wt% and 1.0 wt% solutions were 3780% and 2690%, respectively. The decreasing trend is attributed to the charge-screening effect of the added cations. The cations shield the –COO[–] anions and suppress electrostatic repulsion among the anions, preventing the hydrogels from swelling (Chang et al., 2011; Wu et al. 2012). The cationic valence also exhibited a significant influence on the swelling ability of the D1C1-1 hydrogel. The swelling ratio decreased with increasing cationic valence: 3490, 2690, and 1590% in 1 wt% KCl, CaCl₂, and FeCl₃ solutions, respectively. The multivalent cations (Ca²⁺ and Fe³⁺) could be integrated with the –COO[–] anions of the D1C1-1 hydrogel to establish a denser network structure, resulting in a smaller swelling ratio (Qi et al. 2015; Wu et al. 2012).

The dextran, D1C1-1, and CMC hydrogels were oven-dried and re-swollen by immersion in deionized water for three days. The recovery of the oven-dried samples after immersion in water is shown in **Fig. 7a–c**. The oven-dried dextran and D1C1-1 gels recovered to their original shape, size, and transparency, with *R* values of 89.8% and 87.4%, respectively (**Table 2**). However, the oven-dried CMC gel collapsed upon swelling and the *R* value was as low as 49.9% (**Table 2**). Once dried, the re-swelling ratio of the D1C1-1 hydrogel was approximately 16 000%, which is approximately 1.5 times larger than that of the CMC hydrogel (10 800%). Because the CMC hydrogel is hard, it cannot keep up with the rapid volume change upon the absorption of water and collapse. In contrast, the dextran/CMC hydrogel was able to deform plastically, resulting in a large re-swelling ratio.

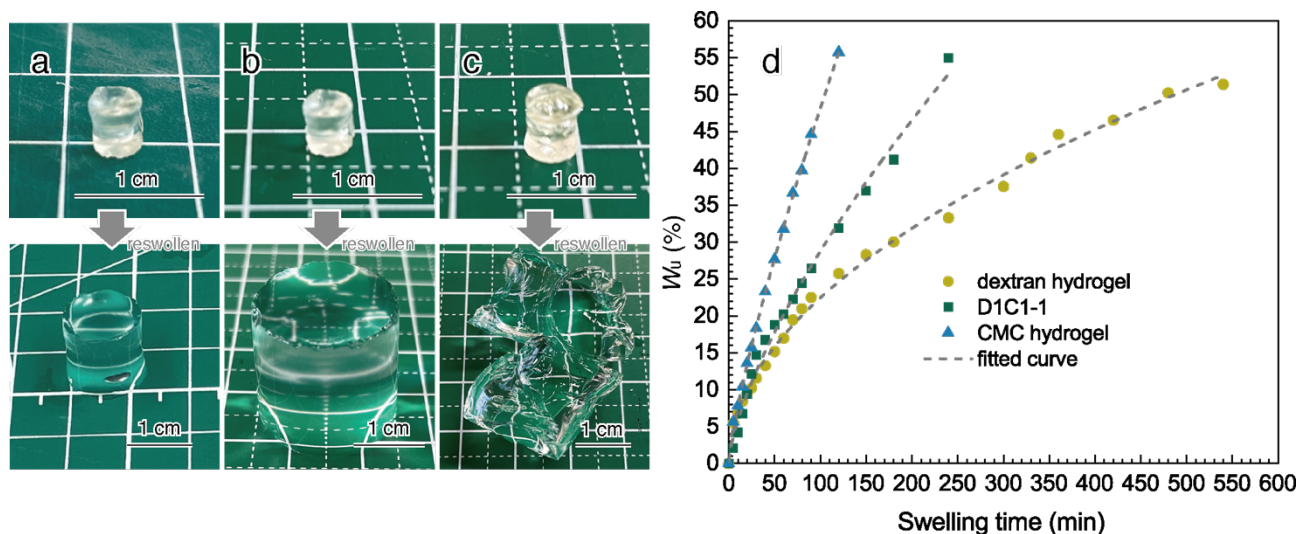


Fig. 7 Images of oven-dried and re-swollen samples of the (a) dextran, (b) D1C1-1, and (c) CMC hydrogels. (d) Dynamic swelling of the hydrogels in deionized water; the W_u values of up to 60% were fitted using the Peppas kinetic equation (Eq. (2)).

Table 2 R values and parameters from the Peppas kinetic equation (k and n) for the dextran, D1C1-1, and CMC hydrogels

Sample	R (%)	k	n	R^2
Dextran hydrogel	89.8	0.022	0.505	0.996
D1C1-1	84.7	0.012	0.693	0.991
CMC hydrogel	49.9	0.012	0.794	0.999

To investigate the mechanism of water diffusion into the dextran, D1C1-1, and CMC hydrogels, the water-swelling kinetics of the oven-dried samples were studied. The dynamic water-swelling data for up to 60% uptake by the hydrogels are shown in **Fig. 7d**. These data were well-fitted to the Peppas kinetic model. The diffusion exponent n , which indicates the transport mechanism, and the diffusion constant k , which relates to the relaxation rate of the hydrogel, were calculated using the least squares method and are listed in **Table 2**. The n values ranged from 0.505 to 0.835, which correspond to non-Fickian diffusion ($0.45 < n < 0.89$) (Khare and Peppas 1995). These values indicate that hydrogel swelling proceeds as the water-swollen region expands into the interior dry region with local deformation. The k values of both the D1C1-1 and CMC hydrogels (0.012) were smaller than that of the dextran hydrogel (0.022). The presence of a carboxyl group in

the molecular chains of the D1C1-1 and CMC hydrogels results in higher swelling rates; however, relaxation of the polymer network is suppressed due to the interaction between the carboxyl groups and water molecules.

Performance of the D1C1-1 hydrogel as an adsorbent

The adsorption of heavy metal ions and dyes on the D1C1-1 hydrogel was investigated using Cu^{2+} and MB solutions, respectively. When the dried D1C1-1 gels were immersed in Cu^{2+} and MB solutions, they fully swelled after 24 h and the gels turned blue and navy blue (**Fig. S2**). The time to reach equilibrium adsorption was set to 3 days. The maximum adsorption peaks at 810 nm and 664 nm for Cu^{2+} and MB solutions, respectively (**Fig. S2**), were used to determine adsorption amount onto the hydrogel.

Adsorption kinetic

Figures 8a and 8b show the kinetics of Cu^{2+} and MB adsorption on the D1C1-1 hydrogel, respectively. The adsorption of Cu^{2+} and MB rapidly increased in the first 200 min and 500 min, respectively, then gradually increased until equilibrium was reached. The experimental kinetics data were fitted with the pseudo-first-order (Eq. (5)) and pseudo-second-order (Eq. (6)) models, and the kinetic parameters were determined (**Table S1**). The adsorption kinetics of Cu^{2+} and MB were slightly better fitted with the pseudo-second-order model than the pseudo-first-order model.

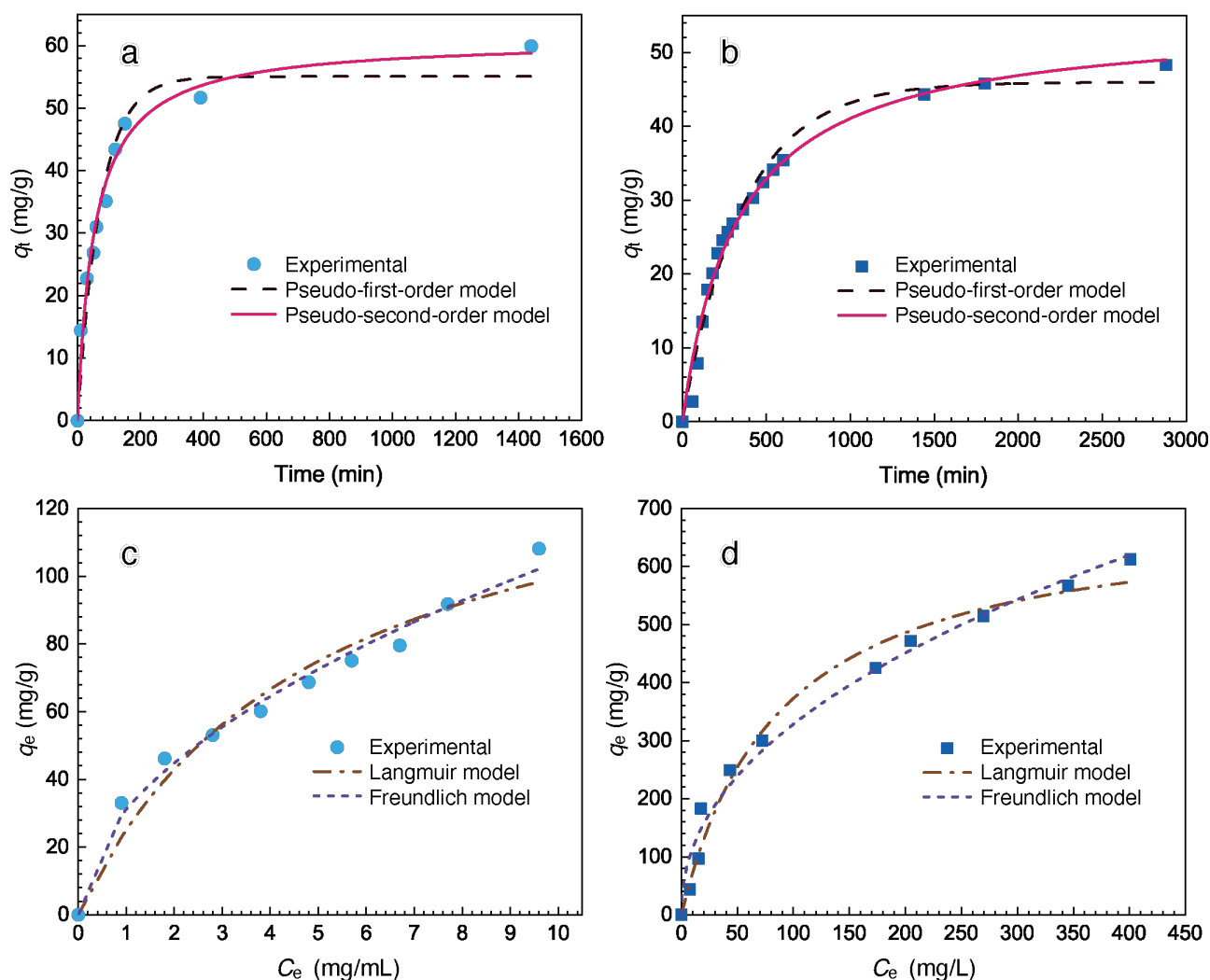


Fig. 8 Kinetics of (a) Cu^{2+} and (b) MB adsorption on D1C1-1 hydrogel. Isotherms of (c) Cu^{2+} and (d) MB adsorption on D1C1-1 hydrogel

Adsorption isotherm

The adsorption isotherms for Cu^{2+} and MB uptake on the dextran, D1C1-1, and CMC hydrogels were investigated using the Langmuir and Freundlich models (**Figs. 8c–d** and **Fig. S3 a–d**), and the adsorption isotherm constants, including the correlation coefficients (R^2), are listed in **Table 3**. The R^2 values were all above 0.9. Therefore, adsorption of Cu^{2+} and MB on the dextran, D1C1-1, and CMC hydrogels were well-fitted with both the Langmuir and Freundlich models. Since there is no clear difference between the Langmuir and Freundlich models, the adsorption mechanism could not be discussed here.

Table 3 Langmuir and Freundlich isotherm constants for adsorption of Cu²⁺ and MB on the dextran, D1C1-1, and CMC hydrogels

Model	Parameter	Cu ²⁺			MB		
		Dextran	D1C1-1	CMC	Dextran	D1C1-1	CMC
Langmuir	q_m	34.04	149.09	156.16	215.42	698.43	789.31
	K_L	0.294	0.202	0.769	0.002	0.011	0.023
	R^2	0.986	0.909	0.976	0.997	0.979	0.946
Freundlich	n	2.224	1.904	3.296	1.517	1.42	2.371
	K_F	9.419	31.13	73.55	1.42	39.81	73.79
	R^2	0.982	0.972	0.997	0.987	0.982	0.969

The maximum adsorption capacities of Cu²⁺ and MB on the D1C1-1 hydrogels were 149.09 mg/g and 698.43 mg/g, respectively. The maximum adsorption capacity of the D1C1-1 hydrogels was three to five times higher than that of the dextran hydrogel because of the presence of the carboxyl groups in the former. The maximum adsorption capacity of the D1C1-1 hydrogel was slightly lower than that of the CMC hydrogel, even though its carboxyl group content was only half of that in CMC. As shown in **Fig. 2a**, D1C1-1 hydrogel have carboxyl groups and hydroxyl groups. There may be two different adsorption mechanism about D1C1-1 hydrogel, namely (1) adsorption onto hydroxyl groups with electrostatic interaction and (2) ion-exchange behavior with carboxylic acid (Isobe et al. 2013). We also measured the adsorption capacity of D1C1-1 hydrogel for Co²⁺ and crystal violet (CV) (**Table S2**), the maximum adsorption capacities of Co²⁺ and CV on the D1C1-1 hydrogels were 65.61 mg/g and 566.69 mg/g, respectively. Comparing the maximum adsorption capacity with that of other polysaccharide-based hydrogels, the D1C1-1 hydrogel showed a high adsorption capacity for Cu²⁺ and MB, whereas the starch-g-poly (acrylic acid)/sodium humate hydrogel showed the highest adsorption capacity for Cu²⁺ (**Fig. S4**).

Reusability

To investigate the reusability of the D1C1-1 hydrogel as an adsorbent, the adsorption–desorption cycle of the D1C1-1 hydrogel was repeated five times after the adsorption of Cu^{2+} and MB (**Fig. S5**). The adsorption capacity was 98.5% for both Cu^{2+} and MB after one cycle, and was maintained at 91.6% and 80.6%, respectively, even after five cycles. These results indicate that the D1C1-1 hydrogel has excellent regeneration properties and the potential for repeated use as an adsorbent.

Conclusion

Transparent, highly swellable, and self-standing hydrogels were prepared from enzymatically synthesized branchless dextran and CMC by crosslinking with EGDE. Upon mixing CMC with dextran, the hydrogel became softer and more flexible than the CMC hydrogel, and its mechanical properties could be manipulated by varying the mixing ratio. After the dextran/CMC hydrogel was dried and immersed in deionized water, it could be restored to its original shape and size, with a recovery ratio of >85%. In contrast, even though the dried sample of the CMC hydrogel re-swelled, it disintegrated when immersed in water. The re-swelling ratio of the dextran/CMC hydrogel was approximately 1.5 times larger than that of the CMC hydrogel. The adsorption isotherm experiments showed that the maximum adsorption capacities of Cu^{2+} and MB on the dextran/CMC hydrogel were maintained at 96% and 88% of those on the CMC hydrogel, respectively. The results of the repeated adsorption/desorption tests demonstrated the reusability of the dextran/CMC hydrogel. In conclusion, the dextran/CMC hydrogel is easy to handle and can be used as an adsorbent material.

CMC is known to be degraded by cellulases (Benoit et al.1995), and degradability of CMC hydrogels are decreased with increasing crosslinking density (Kono et al. 2014). The dextran/CMC hydrogels are biodegradable, and the degradability would be controlled by the mixing ratio of dextran and CMC, the crosslinking density, and the type and concentration of enzymes. Dextran is also degraded by dextran-1,6-glucosidase and dextranase in the human body (Baldwin et al. 2010). The dextran/CMC hydrogel, which possess pH-dependent swelling characteristics, have potential as a drug delivery material. Future studies required to evaluate the biocompatibility and biodegradability of this hydrogel in the human body.

CRediT authorship contribution statement

Yangyang Zhang: Writing - original draft, Investigation, Data curation. **Qinfeng He:** Methodology, Investigation. **Kayoko Kobayashi:** Methodology, Investigation. **Ryosuke Kusumi:** Methodology, Investigation. **Masahisa Wada:** Writing - review and editing, Conceptualization, Methodology, Supervision, Funding acquisition.

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