Highly-porous uniformly-sized amidoxime-functionalized cellulose beads prepared by microfluidics with N-methylmorpholine N-oxide

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Abstract: Uniformly-sized porous cellulose beads functionalized with amidoxime groups were prepared for the first time using a microfluidic method with N-methylmorpholine N-oxide (NMMO) monohydrate as a cellulose solvent. The molten state cellulose dope in NMMO monohydrate (cell/NMMO dope) as a disperse phase and hot mineral oil as a continuous phase were used in a T-junction microfluidic chip to produce uniformly-sized cell/NMMO droplets. Coagulation of the molten state cell/NMMO droplet at high temperature and amidoxime functionalization could prepare the highly-porous spherical amidoxime-functionalized cellulose beads with a uniform fibrous open internal structure. The prepared amidoxime-functionalized cellulose beads showed excellent metal adsorption properties with a maximum adsorption capacity of ~80 mg g\(^{-1}\) in the case of Cu\(^{2+}\)/phthalate ions. The newly developed highly-porous cellulose beads can open many new applications with other proper functionalization at the reactive hydroxyl groups of the cellulose.

Keywords: cellulose, microfluidics, N-methylmorpholine N-oxide, amidoxime, metal adsorption, filter

Introduction

Cellulose, a linear polysaccharide, is the most abundant and renewable biopolymer in nature (Klemm et al. 2011) and has been widely studied because of its unique properties, such as biocompatibility, biodegradability, eco-friendliness, cost-effectiveness, and easy modification. This natural polymer cannot be melted (by heating) and solubilized (in common organic solvents) because of its strong intra- and interchain hydrogen bonding. The cellulose can be a processible liquid form by derivatized chemical modification or direct dissolution with specific solvents. Traditional viscose technology uses derivatization in which cellulose xanthogenate is formed as an intermediate derivative. However, this process produces environmentally hazardous byproducts such as carbon disulfide and hydrogen sulfide (Fink et al. 2001). The direct dissolution process is
purely physical without any structural changes (Rosenau et al. 2002). Of the many solvents for
direct dissolution, N-methylmorpholine N-oxide (NMMO) is a well-known commercialized
solvent (Lidhure et al. 2019). Nontoxic NMMO is economically favorable because it is mostly
recycled and reusable (Dawson 2012; Rosenau et al. 2001). NMMO is used in hydrated forms to
dissolve cellulose. According to the phase diagram of the NMMO/water/cellulose mixture, the
NMMO monohydrate can dissolve cellulose up to 13 wt% (Lidhure et al. 2019). The melting
temperature of the NMMO monohydrate is ~76°C; therefore, the NMMO monohydrate should be
heated to ~80°C to make the cellulose/NMMO (cell/NMMO) dope. Upon cooling, the cell/NMMO
dope becomes solid at temperatures between 20°C and 40°C (Biganska et al. 2002).

Cellulose and cellulose derivatives have been used as adsorbents in the form of hydrogels,
films, beads, microfibers, and microcrystals (Hua et al. 2019). The cellulose beads can be prepared
by sequentially forming spherical cell/NMMO dope, solidification via temperature decrease, and
coagulation with water (Gericke et al. 2013). The cellulose beads can be used for the stationary
phase in chromatography, protein purification, and drug delivery (Alam et al. 2019). The cellulose
beads prepared from the cell/NMMO dope have much porosity because a large amount of NMMO
is extracted from the cell/NMMO dope during coagulation. Their high porosity enhances the
interfacial area available for interactions with the target molecules when using the cellulose beads
as adsorbents. However, the cellulose beads prepared from lower cellulose concentrations have
weak mechanical properties (although they provide high porosity); therefore, crosslinking is
necessary to enhance mechanical properties. The temperature and composition of the coagulation
medium also influence the morphology, internal surface area, and pore size distribution. Hence, to
take full advantage of cellulose beads, the porosity and surface area should be controlled and
optimized with coagulation conditions because they determine the adsorption capacity of the
cellulose beads. The size of the cellulose bead depends on the manufacturing method such that
conventional dropping and dispersion techniques produce cellulose droplets with a size above and
below ~350 μm, respectively, with a certain size distribution (Gericke et al. 2013; Rosenberg et al.
2007). Recently, the microfluidic method has become common for producing uniformly-sized
particles. However, in our limited knowledge, highly controlled manufacturing methods for
producing cellulose beads using microfluidics have not yet been developed using NMMO
monohydrate as a solvent of cellulose.

The pollution of water resources with harmful metals, such as lead, mercury, cadmium,
copper, iron, and chromium, is a serious threat to humans (Sharma et al. 2007). Thus, detecting
and removing such harmful metals in water has been critical for modern society. Various efficient
but expensive methods are proposed to remove heavy metal ions from industrial effluents using
ion-exchange, reverse osmosis, and electrodialysis techniques (Bolto and Pawłowski 1987;
Geckeler et al. 1988; Pawlowski 2015). Chemical precipitation is promising, but the generation of
precipitated bulky hydroxides is often a major disadvantage. Functional cellulose beads were
prepared as biocompatible adsorbents for water treatment using chemical functionalization or
blending cellulose with organic and inorganic compounds. For example, the cellulose beads
carrying carboxylate groups possess high adsorption capacity for calcium, copper, silver, and lead
(Hirota et al. 2009), and those prepared by blending using alginate or chitosan were applied for
removing cadmium and copper (Twu et al. 2003; Zhang et al. 2005). The cellulose modified using amine-containing functional groups (aminooalkyl and 2, 2’-diaminodiethylamine) or an anionic moiety (phosphate, thiolate, carboxyl, and carboxymethyl) has been reported for applications to metal adsorption (Saliba et al. 2000a). Strong fixation of metal ions, especially multivalent ones, to cellulose beads has been achieved by coupling with specific ligands that possess multiple functional groups for metal complexation (Diviš et al. 2009; Matúš and Kubová 2005). Several chelating ligands such as diamines, iminodiacetic acid, or ethylenediaminetetraacetic acid have been coupled to cellulose beads (Boeden et al. 1991; He et al. 1999; Kahovec et al. 1980; Yeomans-Reina et al. 2001). The cellulose beads functionalized with amidoxime groups were also used as metal adsorbents (Saliba et al. 2000b). Amidoxime groups have hydroxyamino (=N–OH) and amino (–NH₂) groups at the same carbon atom, offering the fused features of amide, oxime, amidine, and hydroxamic acid functionality (Li et al. 2013b). Adsorption occurs through sharing or exchanging electrons between the transition metal ions and amidoxime ligand (Rahman et al. 2016; Wang et al. 2015). Amidoxime groups have no affinity for the common metallic cations (Na⁺, K⁺, Ca²⁺, and Mg²⁺) but have a strong tendency to form a chelate complex with various transition and heavy metal ions (Pb²⁺, Cu²⁺, Fe³⁺, and Cd²⁺) in an aqueous solution. The selective chelation of metal cations of the amidoxime group has been widely applied for fabricating functional materials. For example, chelating resins, gels, fibers, microbeads, and membranes functionalized with amidoxime groups were prepared for removing heavy toxic metal ions, enriching and selective recovery of precious metals from natural water and industrial wastewater, and detecting heavy metal ions (Li et al. 2013a). The amidoxime-functionalized materials also have potential applications in CO₂ capture and storage (Zulfiqar et al. 2011).

In this study, uniformly-sized, highly-porous, expandable, and amidoxime-functionalized cellulose (O-cellulose) beads were prepared with the cell/NMMO dope using a microfluidic method. Here stable cell/NMMO droplets in mineral oil were produced with T-junction at 80°C, followed by coagulation in THF/water mixture, crosslinking with epichlorohydrin, and amidoxime functionalization. The structures of the produced cellulose depended on the state of the cell/NMMO droplet (solid or molten) and the temperature of the coagulation bath (hot or cold). The relationship between the internal structure and adsorption properties was studied using samples prepared from a critical point drying (CPD) method with liquid CO2. The prepared O-cellulose beads showed high affinity to multivalent metal ions that were studied by Langmuir isotherm. The relationship between the internal structure and adsorption property was established, with the cellulose beads having various porous structures prepared by different coagulation conditions. The uniformly-sized porous cellulose beads can be easily expanded to other applications because of the easy introduction of different functional groups.
Experimental

Materials

Cellulose powder and NMMO monohydrate were obtained from KOLON (South Korea), and epichlorohydrin (ECH) and acrylonitrile (AN) were purchased from Daejung (South Korea). Sodium hydroxide (NaOH), sodium carbonate (NaCO₃), hydroxylamine hydrochloride (NH₂OH·HCl), tetrahydrofuran (THF), methanol (MeOH), and potassium hydrogen phthalate (KHP) were purchased from Duksan. Tetramethylammonium (TMA) chloride ((CH₃)₄N⁺Cl⁻), copper(II) nitrate hexahydrate (Cu(NO₃)₂·6H₂O), cadmium(II) nitrate (Cd(NO₃)₂), and iron(III) chloride hexahydrate (FeCl₃·6H₂O) were purchased from Junsei (Japan). Lead(II) nitrate (Pb(NO₃)₂), nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O), calcium(II) nitrate tetrahydrate (Ca(NO₃)₂·4H₂O), zinc(II) nitrate hexahydrate (Zn(NO₃)₂·6H₂O), and chromium(II) chloride hexahydrate (Cr(NO₃)₂·6H₂O) were purchased from Sigma Aldrich (USA). All chemicals were used as-received without further purifications.

Preparation of uniformly-sized cellulose droplets

Scheme 1a summarizes the overall schematics of producing cellulose beads using microfluidics. The following is a detailed description of the preparation procedure. The NMMO monohydrate (100 g) was melted in a round-bottom glass tube (outer diameter = 60 mm, length = 180 mm) at 80°C in which the cellulose powders (4 g) were dissolved using a screw-type propeller (diameter = 125 mm, pitch = 35 mm) at 80°C for 2 h. The dissolved cell/NMMO dope was degassed by maintaining it at 90°C for 2 h with a rubber cap on the top to prevent water evaporation in the NMMO monohydrate. The degassed dope was transferred to a plastic syringe (inner diameter = 20.05 mm) to use as a dispersed phase (DP) in microfluidics. Mineral oil with EM90 (3 wt%) in a plastic syringe (inner diameter = 15.90 mm) was used as a continuous phase (CP). The CP and DP were connected to the T-junction microfluidic chip (PEEK, P-713, IDEX, USA), (thru-hole diameter = 1.25 mm) with two separated syringe pumps (LEGATO 100, KD Scientific, USA).

A syringe containing the cell/NMMO dope and the T-junction microfluidic chip is in a bath filled with ethylene glycol at 85°C (Scheme 1a). The flowrates of the DP and CP (Qd and Qc) were controlled at 2.0 and 23 μL min⁻¹, respectively, unless otherwise mentioned. When the cell/NMMO dope meets at the edge of the T-junction, the cell/NMMO droplet was formed. Four cellulose beads samples were prepared, depending on the cell/NMMO droplet’s state during coagulation and coagulation temperature. The cell/NMMO droplet during coagulation can be a solid state (S) or molten state (M). The S cell/NMMO droplets were prepared by cooling the M cell/NMMO droplets in the CP of hot mineral oil by mixing them with a significant amount of cold mineral oil in a beaker that was placed into an ice-water bath before. The cell/NMMO droplets were coagulated at low S and high M coagulation temperatures, representing the S and M of NMMO monohydrate, respectively. The S cell/NMMO droplets were coagulated by removing
the mineral oil from the beaker containing the S cell/NMMO droplets, refilling the beaker with
THF to mix with the remaining mineral oil, removing THF, refilling the beaker with water at 30°C
(S) or 60°C (M), and maintaining them for 30 min. The M cell/NMMO droplets were coagulated
using the following method. The CP hot mineral oil (85°C) containing the M cell/NMMO droplets
appearing from the microfluidic chip was directly dropped into the THF/water mixture (50/50, v/v)
at 30°C (S) or 60°C (M). The THF/water mixture was used during coagulation because the CP
mineral oil containing the cell/NMMO droplets could not be removed in the water bath because of
the immiscibility between water and mineral oil. The coagulated cellulose spherical beads were
filtered using filter papers (Advantec, 110 mm) and washed with water several times. The
produced cellulose beads are denoted as cellulose (S-S), (S-M), (M-S), and (M-M) beads, where
the first S and M represent the solid and molten states of the cell/NMMO droplet, respectively, and
the second S and M represent cold and hot coagulation temperatures, respectively.

(a) State of cell/NMMO droplet

(b) Coagulation condition

CP: Mineral oil/EM 90(3wt%) DP: cellulose/NMMO dope EG: ethylene glycol

CP hot cell/NMMO droplet in CP

Melt-state

Melt-state

Solid-state

Solid-state

Removing CP

Cold water

Hot water

Cellulose (S-S) bead

Cellulose (M-M) bead

Cellulose (S-S) bead

Cellulose (M-M) bead

CP

Cooling with ice bath

CP

Cold THF/water

Hot THF/water

Cellulose (M-S) bead

Cellulose (M-S) bead

NaOH, 55 °C

ECH

X-cellulose

NaOH / TMA / MeOH

25 °C

AN

CN-cellulose

NH₂OH

DIW, 75 °C

O-Cellulose

R₁ = H or CH₃CH₂CN

R₂ = H or
Scheme 1. (a) The overall schematics of producing cellulose (S-S), cellulose (S-M), cellulose (M-S), and cellulose (M-M) beads using a T-junction microfluidic chip at 85°C. CP and DP are continuous and disperse phases, respectively. (b) Crosslinking (X-cellulose) and functionalization with AN (CN-cellulose) and NH₂OH (O-cellulose) to incorporate amidoxime groups in the cellulose beads.

Preparation of O-cellulose beads

The cellulose beads were crosslinked with ECH (Scheme 1b). The ECH reacting with hydroxyl groups of the cellulose introduces oxirane moieties that can further react with hydroxyl groups of the same or another cellulose chain nearby (Gough 1967). The detailed reaction conditions are as follows. Briefly, the cellulose beads (0.1 g) were dispersed in an aqueous NaOH solution (3 wt%, 20 mL) under magnetic stirring for 30 min. The ECH/MeOH (3.08 g (1.54 g each), 1:3 mole ratio of anhydrous glucose unit (AGU):ECH) was added dropwise, under magnetic stirring at 60°C for 1 h. After the reaction, the reaction medium was washed with water until a pH 7. The crosslinked cellulose (X-cellulose) beads were dried at 25°C for 2 h in a vacuum oven. The amidoxime groups were introduced into the cellulose beads (Scheme 1b). The dried X-cellulose beads were further functionalized with AN to introduce the −CN groups as follows. Briefly, the X-cellulose beads (0.1 g (0.55 mM)) were dispersed in 20 mL AN into which a 0.56 mL MeOH solution containing 5 wt% TMA chloride was added. A 0.75 mL MeOH solution containing 10 wt% sodium hydroxide at 0°C was added dropwise. The reaction was maintained at 25°C for 2 h under magnetic stirring and finally, washed with water until the medium’s pH reached 7. The CN-functionalized cellulose (CN-cellulose) beads were further reacted with NH₂OH-HCl to introduce the amidoxime groups as follows. NH₂OH-HCl (8 g), Na₂CO₃ (6 g), and CN-cellulose beads (0.1 g) were added to a 250 mL beaker, to which 100 mL water was added and sealed. The reaction was maintained at 70°C for 12 h. After the reaction, the O-cellulose beads were washed several times with water to remove the remaining salts. Water was replaced with MeOH, and the O-cellulose beads were dried in a vacuum oven at 25°C.

Critical point drying

To prepare cellulose bead samples for scanning electron microscope (SEM) and porosity/inner surface area determination, the CPD method with liquid CO₂ was used (Pinnow et al. 2008; Trygg et al. 2013) because the simple evaporation of water by vacuuming, heating, and air-drying results in the hornification of the bead surface and loss of their significant porosity and surface area (Gericke et al. 2013). Lyophilization (freeze-drying) also causes water volume expansion upon freezing and the growth of ice crystals, resulting in a micro- and mesopore collapse in cellulose beads (Pinnow et al. 2008). For CPD with liquid CO₂, water should be stepwise exchanged by ethanol, acetone, and liquid CO₂, which is removed under supercritical conditions. To investigate
the internal structure of the prepared cellulose beads using the CPD method, the CPD container was home-made (Fig. S1). Detail CPD procedures can be found in Text S1.

**Measurements**

Attenuated total reflection (ATR)–Fourier transform infrared (FTIR) (ATR–FTIR) spectra were recorded in the range of 500–4000 cm\(^{-1}\) at an average of 64 scans using an FTIR spectrometer (Frontier, PerkinElmer, USA). The dried samples were ground into a fine powder using a pestle and mortar. Field-emission (FE)-SEM (FE-SEM; SU8220, Hitachi, Japan) images of the cellulose beads were obtained from the fractured surfaces of the platinum-coated epoxy-molded samples. The samples for SEM were dried using the CPD method with liquid CO\(_2\). The epoxy molding was performed by positioning the beads in the cap (Cavity Embedding Mold, Ted Pella, USA), filling the cap with an epoxy mixture of EPON (2 mL), DDSA (1.25 mL), NMA (1.25 mL), and DMP (0.075 mL), curing at 60°C for 24 h, and breaking by half with a vise. The cellulose beads were observed using an optical microscope (ANA-006, Leitz, Germany) equipped with a digital camera (STC-TC83USB-AS, SenTech, Japan) with a transmission mode. The Cu\(^{2+}\)/phthalate solution concentration was determined using ultraviolet (UV)–visible (vis) (UV-vis) spectroscopy (UV-2401PC, Shimadzu, Japan). The chemical composition of the cellulose beads was studied using an elemental analyzer (EA, Flash 2000, ThermoFisher, USA). The concentrations of the metal ions in water were investigated using an inductively-coupled plasma spectrometer (ICP, Optima 7300DV, PerkinElmer, USA). The surface area of the cellulose beads (S-S, M-M) was determined using a surface area and pore size analyzer (Quadrasorb Evo, Quantachrome, Austria) using the Brunauer–Emmett–Teller (BET) method. The samples for BET analysis were dried using the CPD method with liquid CO\(_2\) and pre-treated at 100°C for 12 h in a vacuum oven.

**Adsorption of metal ions**

A Cu\(^{2+}\)/phthalate complex aqueous solution was used to demonstrate the O-cellulose beads’ performance on the Cu\(^{2+}\) ion detection using UV-vis spectroscopy. It was prepared by dissolving Cu(NO\(_3\))\(_2\) (controlled from 50 to 1000 ppm) and KHP (4.08 g, 0.2 M, excess) in water (100 mL). Fig. S2(a) shows the UV-vis spectra of the Cu(NO\(_3\))\(_2\) (1000 ppm), KHP (0.2 M), and Cu\(^{2+}\)/phthalate (1000 ppm/0.2 M) complex aqueous solutions. The Cu(NO\(_3\))\(_2\) aqueous solution’s UV-vis spectrum shows a small peak at 780 nm. However, the Cu\(^{2+}\)/phthalate complex aqueous solution’s UV-vis spectrum shows a strong absorption peak at 730 nm with a hypochromic shift, consistent with reported results (Saliba et al. 2000b). The Cu\(^{2+}\)/phthalate complex aqueous solution’s calibration curve (730 nm) was obtained at different concentrations with a linear regression curve (\(r^2 = 0.998\)) (Fig. S2(b)). Each adsorption experiment was conducted thrice to investigate the adsorption behavior of metal ions onto the cellulose bead adsorbent. The concentrations of the aqueous metal-ion solutions before and after adsorption were measured using...
a UV–vis spectrophotometer (UV-1800, Shimadzu Corporation, Japan) at a wavelength range of 400–800 nm. The adsorption capacity \( q_t \) for the Cu\(^{2+}\)/phthalate complex was evaluated using equation (1).

\[
q_t = \frac{(C_0-C_t) \times V}{m}
\]  

(1)

where \( C_0 \) (mg L\(^{-1}\)) and \( C_t \) (mg L\(^{-1}\)) are the dye concentrations at the initial time and time \( t \), respectively. \( V \) (L) is the volume of the dye solution, and \( m \) (g) is the weight of the dried adsorbent.

### Desorption of metal ions

For the desorption experiment, the metal-ion-loaded O-cellulose beads were immersed in 8 mL of 2 M HCl for 30 min under magnetic stirring at 25°C, and the O-cellulose beads were regenerated into the initial form after sequentially rinsing with water and pH 6 buffer solution several times. The adsorption test was performed again by magnetic stirring regenerated O-cellulose beads (4 mg) in Cu\(^{2+}\)/phthalate solution (4 mL, 1000 ppm) at pH 7 for 2 h. The adsorption/desorption cycle was repeated five times to investigate the recyclability of the O-cellulose bead.

### Results and discussion

#### Production of cellulose beads using microfluidics

To find the optimum \( Q_d \) and \( Q_c \) in microfluidics, the cellulose (4 wt%)/NMMO dope was evaluated at different \( Q_d \) and \( Q_c \) in the T-junction microfluidic chip. The production of the cell/NMMO droplet in the T-junction microfluidic chip in the ethylene glycol bath could not be monitored in situ through an optical microscope; therefore, the cellulose (M-M) bead’s shape after coagulation was examined as a model study. Fig. 1a shows the matrix diagram of processability at different \( Q_d \) and \( Q_c \). The matrix graph can be divided into three regions representing the non-processible condition (Region I) and conditions for producing asymmetric-prolate (Region II) and symmetric-spherical (Region III) cellulose beads. The inset figures show representative optical microscopy images of the cellulose beads. When \( Q_c > \sim 10.0 \) \( \mu \)L min\(^{-1}\) and \( Q_d > \sim 1.0 \) \( \mu \)L min\(^{-1}\) (Region III), the symmetric-spherical cellulose beads were produced. In the case of 6.0 \( \mu \)L min\(^{-1}\) < \( Q_c < 10.0 \) \( \mu \)L min\(^{-1}\) (Region II), the asymmetric elongated prolate cellulose beads were produced. When \( Q_c < 6.0 \) \( \mu \)L min\(^{-1}\) (Region I), the droplets could not be produced.

At low capillary numbers (low \( Q_d \)) in the T-junction chip, droplets are formed in a squeezing mode, forming a pressure gradient across the droplet as it is formed (Seemann et al. 2011). Droplets generated in the squeezing mode travel through the channel as a plug confined by the channel walls. As the \( Q_c \) increases (i.e., the capillary number increases), droplet generation transits from the squeezing to the dripping mode. It is unclear whether Region III (highest \( Q_c \)) is in the dripping mode or not (Zhu and Wang 2017).
produced at $Q_d = 4 \mu L min^{-1}$ and $Q_c = 30 \mu L min^{-1}$ (high $Q_c$ in Region III) were evaluated at different coagulation temperatures. Figs. 1b and c show the optical microscopy images of the cellulose beads coagulated from the M and S cell/NMMO droplets at different temperatures, respectively. Both M and S cell/NMMO droplets are the same at the T-junction in the microfluidic chip. In the case of the M cell/NMMO droplets (Fig. 1b), ellipsoidal cellulose beads were produced at $T_{coa} = 10^\circ C$, $20^\circ C$, $30^\circ C$, and $40^\circ C$, although spherical cellulose beads were at $T_{coa} > 50^\circ C$. The cellulose beads prepared at $T_{coa} > 50^\circ C$ represent cellulose (M-M) beads. The ellipsoidal shape of the cellulose beads produced at low $T_{coa}$ indicates that the cell/NMMO droplets at the T-junction were produced in the squeezing mode. The shear stress generated at the T-junction of the microfluidic chip during droplet production can be easily released during coagulation in the case of the cellulose (M-M) bead because of high-temperature coagulation of the M cell/NMMO droplet. Thus, spherical cellulose could be observed for cellulose (M-M) beads, although they were formed in the squeezing mode. The squeeze mode is evident from the S cell/NMMO droplets (Fig. 1c). Ellipsoidal cellulose beads were produced at all studied $T_{coa}$ because the ellipsoidal shape of the cell/NMMO droplets at the T-junction was fixed during cooling the cell/NMMO droplets to make the S cell/NMMO droplets. Thus, the cell/NMMO droplets at the T-junction are in the squeezing mode. We could not increase $Q_c$ to reach the dripping mode because of the limitation of the syringe pump because of the high viscosity of cell/NMMO dope.
Fig. 1. (a) Matrix diagram of the formation of cellulose (M-M) beads prepared at different $Q_d$ and $Q_c$ with three regions representing the non-processible condition ($\times$) and the conditions for producing asymmetric-prolate ($\Delta$) and symmetric-spherical cellulose ($\bullet$) beads. (b, c) Optical microscopy images of the cellulose beads coagulated from (b) the M cell/NMMO droplets and (c) the S cell/NMMO droplets coagulated at (i) 10°C, (ii) 20°C, (iii) 30°C, (iv) 40°C, (v) 50°C, and (vi) 60°C. The same scale bar (0.5 mm) is applied to all figures in (b) and (c).

The size distribution of cellulose beads produced under different coagulation conditions was examined. Fig. 2 shows the size distribution of cellulose (S-S), (S-M), (M-S), and (M-M) beads. An ellipsoidal shape is observed from cellulose (S-S), (S-M), and (M-S) beads, whereas a spherical shape is observed from cellulose (M-M) beads, as discussed before. The uniformly-sized ellipsoidal cellulose (S-S), (S-M), and (M-S) beads were obtained with a long axis of $1219.3 \pm 78.7 \mu$m and a short axis of $779.4 \pm 42.9 \mu$m with a narrow size distribution. The spherical cellulose (M-M) beads were obtained with a diameter of $784 \pm 24.8 \mu$m with a narrow size distribution. The cellulose beads coagulated at the molten state (cellulose (S-M) and (M-M)) are whitish compared...
to those coagulated at the solid state (cellulose (S-S) and (M-S)), indicating that the internal
structure coagulated at the molten state is different from that at the solid state. The coagulation
occurs through water diffusion into the cell/NMMO droplet; therefore, the coagulation temperature
is critical to control the internal porous structure of the cellulose bead because the produced
cogulated structure is governed by the rate of water diffusion, which also strongly depends on the
cogulation temperature. The internal structure was studied using a dried sample prepared using
the CPD method.

Fig. 2. Size distribution graphs of the produced (a) cellulose (S-S), (b) cellulose (S-M), (c)
cellulose (M-S), and (d) cellulose (M-M) beads prepared at $Q_d = 4 \mu\text{L min}^{-1}$ and $Q_c = 30 \mu\text{L min}^{-1}$.
The size distribution graphs are for long and short axes of the prolate spheroid in the cases of
cellulose (S-S), (S-M), and (M-S), and the diameter of the sphere in the case of cellulose (M-M).
The inset graphs are photographic images.
Fig. 3. (a) SEM images of the fractured surfaces of the cellulose (i) (S-S), (ii) (S-M), (iii) (M-S), and (iv) (M-M) beads. The samples were dried using the CPD method. The right upper insets are enlarged images of core parts (red square box), and the left upper insets are enlarged images of shell parts (blue square box). (b) The $D_c/D_T$ of cellulose beads prepared from the S (●) and M (○) cell/NMMO droplets as a function of coagulation temperature ($T_{coa}$), where $D_c$ and $D_T$ are the core and total diameters along the short axis, respectively.
Structure of the cellulose bead

Morphologies of the prepared cellulose beads were analyzed with samples dried using the CPD method. Fig. 3 shows the SEM images of the fractured surfaces of cellulose (S-S), (S-M), (M-S), and (M-M) beads. During coagulation, water dilutes the NMMO content in the cell/NMMO droplet, and the diluted NMMO has low solvation power of cellulose, leading the phase separation. For cellulose (S-S) (Fig. 3a(i)) and (M-M) (Fig. 3a(iv)) beads, the internal structures are homogeneous, although the cellulose (M-M) bead is coarser and more porous than the cellulose (S-S) bead. The reason could be that the dissolved cellulose chains in the M cell/NMMO droplet are coagulated (phase-separated) with high mobility to form large phase-separated fibrous bundles in the case of the cellulose (M-M) bead. The surface areas of cellulose (S-S) and (M-M) beads measured using a BET method are 196 and 218 m$^2$g$^{-1}$, respectively, indicating that cellulose (M-M) beads have a more porous structure, consistent with morphology data from SEM. Thus, spherical homogeneous cellulose (M-M) beads with open and porous structures were studied for further tests. For cellulose (M-S) beads (Fig. 3a(iii)), M cell/NMMO droplets were directly dropped into the THF/water mixture (at 30°C) during coagulation. The outer surface of the cell/NMMO droplet in the molten state contacts the cold THF/water mixture in the coagulation beaker; therefore, the outer part of the cell/NMMO droplet becomes solid but the inner part is still in the molten state because the temperature cannot be cooled enough to become a solid state during initial coagulation. Thus, the structure in the outer part of the cellulose (M-S) bead is different from that in the inner part. The outer and inner parts were coagulated in solid and molten states, respectively, so that the structure of the core is coarser than that of the shell, as discussed with cellulose (M-M) and (S-S) beads (Fig. 3a(i), (iv)). For cellulose (S-M) beads (Fig. 3a(ii)), the S cell/NMMO droplet was dropped into hot water (at 60°C) during coagulation; therefore, the S cell/NMMO droplet was changed to the M cell/NMMO droplet by heating through hot water. However, the outer part was coagulated (phase-separated) quickly in the solid state before reaching the melting temperature for the S cell/NMMO droplet, although the thickness of the shell is small (Fig. 3a(ii)). Thus, similar to the cellulose (M-S) beads, the coagulation between the outer and inner parts is different to make the core/shell structure; therefore, the outer and inner parts are coagulated in solid and molten states, respectively.

The effect of the coagulation temperature on the thickness of the shell was studied. Fig. 3b shows the $D_c/D_T$ of cellulose beads (prepared from S and M cell/NMMO droplets) as a function of the coagulation temperature ($T_{coa}$), where $D_c$ and $D_T$ are the core and total diameters (along the short axis), respectively. The $D_T$ and $D_c$ were measured using optical microscopy and SEM images (Fig. S3), respectively, because the samples in epoxy for SEM image were distorted during sample preparation. When $D_c/D_T = 0$ or 1, the cellulose beads are homogenous without a core/shell structure, although they are compact (closed) and coarse (fibrous) in the case of $D_c/D_T = 0$ and 1, respectively, as discussed in cellulose (S-S) and (M-M) beads. The cellulose beads from the S cell/NMMO droplets show the homogenous compact structure ($D_c/D_T = 0$) at $T_{coa} \leq 40^\circ$C (cellulose (S-S) bead) and the core/shell structure at $T_{coa} > 40^\circ$C (cellulose (S-M) bead). The
cellulose beads from the M cell/NMMO droplets show the core/shell structure at $T_{\text{coa}} = 20^\circ\text{C}$–$50^\circ\text{C}$ (cellulose (M-S) bead), and the homogeneous open structure ($D_s/D_T = 1$) at $T_{\text{coa}} = 60^\circ\text{C}$ (cellulose (M-M) bead). Thus, four types of cellulose beads could be made by controlling the cell/NMMO droplet’s state and coagulation temperature and the $T_{\text{coa}}$ can control the thickness of the shell.

**Preparation of O-cellulose beads**

The coagulated cellulose beads in water before drying had almost the same size as the cell/NMMO droplet. Thus, the dried cellulose beads should be shrunk significantly from the cellulose bead in the water because the solid content in the dope is only a few percent. When the dried cellulose bead is inserted into the water again for adsorption applications, the reswelling of the dried cellulose bead is critical to use as an adsorbent with a large surface area inside the cellulose bead. Fig. S4a shows the optical microscopy images of cellulose (M-M) beads without crosslinking before (in water) and after drying and reswelling of the dried cellulose beads. The completely dried cellulose did not swell to the original cellulose bead in the water, indicating that the hydrogen bonding bonds formed after drying prevent the reswelling of the dried cellulose beads. Fig. S4b shows the optical microscopy images of cellulose (M-M) beads with crosslinking. The completely dried cellulose beads swelled to the original cellulose bead in water, indicating that the crosslinking prevents hydrogen bonding formation after drying (Udoetok et al. 2016). Thus, crosslinking the cellulose bead promotes both stability and expansion ability. The degree of reswelling of the cellulose bead depended on the cellulose concentration in the dope, which will be discussed in a later section.

Table 1 shows the diameters of the X-cellulose beads prepared at different cellulose concentrations in the dope before (in water) and after drying, and after reswelling of the dried cellulose beads. The diameters of the swollen, dried, and reswollen X-cellulose beads are denoted as $D_1$, $D_2$, and $D_3$, respectively. The diameter of the dried X-cellulose bead ($D_2$) increases as $\phi$ increases because the solid content in the cell/NMMO droplet increases as $\phi$ increases. However, the ratio between reswollen and dried cellulose beads ($D_3/D_2$) decreases as $\phi$ increases. When crosslinking is performed at low $\phi$, it effectively blocked the hydrogen bonding; therefore, the small collapsed dried X-cellulose beads (because of low $\phi$) can be swollen much but less than the original size before drying. Accordingly, the $D_3/D_2$ becomes larger as $\phi$ decreases. However, the X-cellulose beads prepared at $\phi = 2$ and 3 wt% cannot be reswollen to the original size in water, but at $\phi = 4$ and 5 wt% reswelled to close to the original size ($D_3/D_1 = 0.5, 0.7, 0.9$, and 1 at $\phi = 2, 3, 4, \text{and} 5$ wt%, respectively. When $\phi$ increases to 5 wt%, droplet fabrication became challenging because of its high viscosity. Thus, the X-cellulose beads prepared at $\phi = 4$ wt% were used for further experiments.
Table 1. Diameters of the X-cellulose beads prepared at different ϕ before (in water) and after
drying, and after reswelling of the dried cellulose beads. The diameters of the swollen, dried, and
reswollen X-cellulose beads are denoted as D₁, D₂, and D₃, respectively. The diameter of the initial
cellulose beads before crosslinking is 784 ± 24.8 μm for all ϕs.

| Dope Concentration (ϕ) (wt%) | Swollen X-cellulose (D₁) (μm) | Dried X-cellulose (D₂) (μm) | Reswollen X-cellulose (D₃) (μm) | Diameter Ratio (D₃/D₂) (Volume Ratio) |
|-----------------------------|-------------------------------|-------------------------------|-------------------------------|--------------------------------------|
| 2                           | 800                           | 100                           | 400                           | 4 (64)                               |
| 3                           | 750                           | 200                           | 500                           | 2.5 (16)                             |
| 4                           | 650–750                       | 250                           | 580–700                       | 2.3 (12.2)                          |
| 5                           | 550–650                       | 300                           | 550–600                       | 1.8 (5.8)                           |

The X-cellulose beads were functionalized with AN to make intermediate CN-cellulose beads
that were further functionalized with NH₂OH to make the final O-cellulose beads. FTIR
spectroscopy confirmed the functionalization of X-, CN-, and O-cellulose. Fig. 4a shows the FTIR
spectra of the cellulose, X-cellulose, CN-cellulose, and O-cellulose beads. The FTIR spectrum of
the X-cellulose bead is close to that of cellulose because of the similarity of their functional
groups. The FTIR spectrum of the CN-cellulose shows a characteristic –CN stretching band at
2260 cm⁻¹. The FTIR spectrum of the O-cellulose shows additional peaks at ~920, 1610, and 1670
cm⁻¹ because of the stretching vibration bands of –N=O, –N–H, and –C=O bonds in amidoxime
(Saeed et al. 2008). Thus, the amidoxime groups were successfully introduced into the cellulose
beads. The porous structures were studied using SEM with cellulose (M-M) beads and their
functionalized cellulose beads (X-, CN-, and O-cellulose beads). Figs. 5 b and c show the SEM
images of the outer and fractured surfaces, respectively, of cellulose, X-cellulose, CN-cellulose,
and O-cellulose beads that were dried using the CPD method. The internal structures (from the
fractured surface, Fig. 4c) of all cellulose beads are porous regardless of functionalization,
although the outer surfaces exhibit a small, closed structure (Fig. 4b). The cellulose structure can
easily collapse during the drying process because of the strong hydrogen bonding. The CPD is one
of the best methods to preserve the swollen structure during drying. Thus, the open fibrous
structure of cellulose beads can be observed. However, it is uncertain whether the observed closed
structure from the outer surface is produced during CPD or initially exists because the even CPD
method can cause some hornification during drying. To figure out the origin of this observation, studies are necessary but out of this study’s scope.

Fig. 4. (a) FTIR spectra of the (i) cellulose, (ii) X-cellulose, (iii) CN-cellulose, and (iv) O-cellulose beads. (b, c) SEM images of the (b) outer and (c) fractured surfaces of cellulose (M-M) beads dried using the CPD method; (i) cellulose, (ii) X-cellulose, (iii) CN-cellulose, and (iv) O-cellulose beads. The insets are enlarged images of the red square box.

The degree of conversion from –OH to –CN groups for CN-cellulose beads and from –CN to amidoxime groups for O-cellulose beads were calculated using EA. Table S1 summarizes the EA results of cellulose, CN-cellulose, and O-cellulose beads. The contents of N are 4.31 and 10.05
wt% for CN-cellulose and O-cellulose beads, respectively, although those of C are ~44 ± 3 wt% for all cellulose beads. From EA data, the degree of conversion to –CN groups for CN-cellulose beads and to amidoxime groups for O-cellulose beads was calculated. Scheme S1 shows the chemical structure with x, y, and z where x, y, and z represent the number of –CN groups converted among three –OH groups, the number of converted –CN groups to the amidoxime groups, and the number of unconverted –CN groups, respectively, so that x = z + y. The molecular weights of one unit of CN- and O-cellulose are 180 + 54x and 180 + 54y + 87z, respectively, where 54 and 87 are molecular weights (per mole) of -CH$_2$CH$_2$CN and amidoxime (–CH$_2$CH$_2$C(=NOH)NH$_2$) groups, respectively. The nitrogen contents in weight percentage are 14%/(180 + 54x) × 100 and (28z + 14y)/(180 + 54y + 87z) × 100 for CN- and O-cellulose beads, respectively. The measured nitrogen contents are 4.31 and 10.05 wt% for CN- and O-cellulose beads, respectively, so that the calculated x, y, and z values (with x = y + z) are 1.5, 1.0, and 0.5, respectively. Thus, the degree of conversion from –OH to –CN groups (x) for CN-cellulose beads is 50% (1.5/3 × 100), and from –CN to amidoxime group for O-cellulose is 33% (0.5/1.5 × 100). The degree of conversion of the amidoxime group is similar to the reported value of 40% from amidoxime-functionalized poly(acrylonitrile) (PAN) nanofibers, although it is produced by different reaction conditions with different concentrations of NH$_2$OH·HCl (Saeed et al. 2008).

 Isotherm of the metal-ion on O-cellulose bead

The O-cellulose beads were used as an adsorbent for the Cu$^{2+}$/phthalate complex in water. The Cu$^{2+}$/phthalate complex enhances the intensity of Cu$^{2+}$ in UV-vis spectroscopy, as discussed before. Fig. 5 shows the $q_t$ of the Cu$^{2+}$/phthalate complex on O-cellulose beads as a function of elapsed time ($t_{\text{elapse}}$) at different concentrations. Curve-fitting was performed using equation (3) of the pseudo-first-order kinetics (Fig. 5a) and equation (5) of the pseudo-second-order kinetics (Fig. 5b). The curve-fitted data of $q_t$ and k are the amount of adsorbed material at equilibrium and adsorption kinetic coefficient, respectively. The parameters of $q_{1i}$ and $k_1$ for the first-order kinetics and $q_{2i}$ and $k_2$ for second-order kinetics were calculated using modified equations (4) and (6) with plots of $ln(q_e - q_t)$ vs. $t$ and $t/q_t$ vs. $t$, respectively (Fig. S5). Table S2 summarizes the curve-fitting results with parameters $q_e$, $k$, and $r^2$. The observed data are better curve-fitted with the second-order equation (5) than the first-order equation (3). $r^2$ are 0.9610 and 0.9919 for the first- and second-order equations, respectively. These results indicate that the adsorption mechanism is because of the chelating reaction between the transition metal ions and the amidoxime group (Rahman et al. 2016; Wang et al. 2015).

$$q_t = q_e(1 - e^{-k_1t})$$  \hspace{1cm} (3)

$$ln(q_e - q_t) = -k_1t + lnq_e$$  \hspace{1cm} (4)

$$q_t = \frac{q_e^2k_2t}{1+q_e^2k_2t}$$  \hspace{1cm} (5)
\[
\frac{t}{q_t} = \frac{1}{q_{e2}k_2} + \frac{t}{q_{e2}}
\]  

(6)

Fig. 5. \(q_t\) of the Cu\(^{2+}\)/phthalate adsorption (at different concentrations) on O-cellulose beads prepared with cellulose (4 wt%)/NMMO droplets as a function of elapsed time \((t_{\text{elap}})\) with curve-fitting using (a) equation (3) of the pseudo-first-order kinetics and (b) equation (5) of the pseudo-second-order kinetics.

The isotherm was performed using Langmuir (equation (7)) and Freundlich (equation (9)) models, where \(q_m\) is the adsorption capacity (related to the number of available binding sites), \(C_e\) is the aqueous phase concentration at equilibrium, \(K_L\) and \(K_F\) are the affinity constants for adsorption for the Langmuir (equation (7)) and Freundlich (equation (9)) models, respectively, and \(n\) is the index of heterogeneity. The parameters in equations (7) and (9) were calculated by performing linear curve fittings with modified Langmuir and Freundlich isotherm equations (8) and (10) with the Cu\(^{2+}\)/phthalate complex at a concentration range of 25–1000 ppm at 25°C (Fig. 6). Table S3 summarizes the calculated \(q_m, K,\) and \(n\). The \(r^2\) values of the Langmuir and Freundlich isotherm curves are 0.99 and 0.95, respectively, indicating that the Langmuir model is well-fitted with observed data and a saturated monolayer (not multilayer) of solute molecules on the adsorbent surface was formed during adsorption. The affinity constant of \(K_L\) is 0.013 L·mg\(^{-1}\), similar to the reported value (0.014 L·mg\(^{-1}\)) from poly(amidoxime) cellulose powder (Rahman et al. 2018). The calculated \(q_m\) is ~81.30 mg g\(^{-1}\), which is larger than the reported value (52.70 mg g\(^{-1}\)) from amidoxime-functionalized poly (acrylonitrile) (PAN) nanofibers with an oxime group conversion of 25% (Saeed et al. 2008). Thus, the prepared O-cellulose beads from cellulose (M-M) beads have large adsorption capability of metal ions.

\[
q_e = \frac{K_Lq_mC_e}{1+K_LC_e}
\]  

(7)

\[
\frac{C_e}{q_e} = \frac{1}{q_mC_L} + \frac{C_e}{q_m}
\]  

(8)

\[
q_e = K_F C_e^{1/n}
\]  

(9)

\[
\log q_e = \log K_F + \frac{\log C_e}{n}
\]  

(10)
Fig. 6. (a, c) Isotherm curve and (b, d) its linear curve-fitting using modified equations (8) and (10) for (a, c) Langmuir and (b, d) Freundlich models for adsorption of Cu^{2+}/phthalate complex on O-cellulose beads. The solid lines (a, c) represent the calculated graphs of equations (7) and (9), respectively, with parameters obtained from linear regressions of (b, d).

Internal structure and adsorption property relationship

The O-cellulose beads made from cellulose (S-S), (S-M), and (M-S) beads were also evaluated as adsorbents for the Cu^{2+}/phthalate complex in water to establish the relationship between the internal porous structure and adsorption property. Fig. 7a shows the $q_t$ of O-cellulose beads made from cellulose (S-S), (S-M), (M-S), and (M-M) beads 40 h after O-cellulose beads (4 mg) were inserted into the vials containing the Cu^{2+}/phthalate complex (1000 ppm, 4 mL). The measured $q_s$ are 61.2, 66.8, 69.9, and 83.0 mg g$^{-1}$ for O-cellulose beads prepared from cellulose (S-S), (S-M), (M-S), and (M-M) beads, respectively. The O-cellulose beads prepared from cellulose (M-M) beads have the highest adsorption capacity because it has the highest porous structure, as discussed before, and vice versa for O-cellulose beads prepared from cellulose (S-S) beads. The O-cellulose beads prepared from cellulose (S-M) and (M-S) beads have adsorption capacity between them. Thus, we found that the internal structure of O-cellulose beads governs the adsorption capacity.
Application to fillers in the column

The O-cellulose beads were applied to fillers in a column as an application to a metal filter. The uniformly-sized O-cellulose beads could be packed into the column (Fig. S6). Fig. 7b shows the concentration reduction of the Cu\(^{2+}\)/phthalate complex aqueous solution (initial concentration; 500 ppm) as a function of the cycle number by passing the complex solution (4 mL) through the column (diameter 5.6 mm) filled with the O-cellulose beads (70 mg) with a flow rate of 2.5 mL h\(^{-1}\). The Cu\(^{2+}\)/phthalate complex aqueous solution was circulated for the cycling test using a syringe pump. The initial Cu\(^{2+}\)/phthalate complex aqueous solution (500 ppm) concentration was reduced by 324, 409, 442, and 470 ppm during the first, second, third, and fourth cycles. The percentages of the reduction are 64.8%, 81.8%, 88.4%, and 94% during the first, second, third, and fourth cycles. The amount of O-cellulose beads in the column is only 0.07 g, and 94% of the metal-ion was filtered after the fourth cycle. The results indicate that O-cellulose beads can be successfully used as fillers in the column for metal adsorption.

Other metal-ion adsorptions were studied using ICP. The Pb\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Ni\(^{2+}\), Cd\(^{2+}\), Fe\(^{3+}\), Ca\(^{2+}\), Cr\(^{3+}\), and Mg\(^{2+}\) aqueous solution was prepared with the same concentration of 1000 ppm. Their concentrations were measured 24 h after O-cellulose beads (4 mg) were inserted into the vial containing the metal-ion solution (4 mL). Fig. S7 shows the adsorption capacity of Pb\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Ni\(^{2+}\), Cd\(^{2+}\), Fe\(^{3+}\), Ca\(^{2+}\), Cr\(^{3+}\), and Mg\(^{2+}\) ions, which are 125.0, 75.1, 62.5, 51.1, 34.5, 33.4, 11.1, and 0 mg g\(^{-1}\), respectively, indicating that O-cellulose beads can remove hazardous metal ions. The order of the adsorption amount is Pb\(^{2+}\) > Cu\(^{2+}\) > Zn\(^{2+}\) > Ni\(^{2+}\) > Cd\(^{2+}\) > Fe\(^{3+}\) > Cu\(^{2+}\) > Cr\(^{3+}\) = Mg\(^{2+}\) (not adsorbed). The Pb\(^{2+}\) is adsorbed most and Ca\(^{2+}\), Cr\(^{3+}\), and Mg\(^{2+}\) cannot be adsorbed on O-cellulose beads, similar to other reported results (Rahman et al. 2016; Saeed et al. 2008).

The desorption and re-adsorption of the Cu\(^{2+}\)/phthalate on O-cellulose beads were studied. The O-cellulose beads (4 mg) in the vial were evaluated with the Cu\(^{2+}\)/phthalate aqueous solution. The 1000 ppm Cu\(^{2+}\)/phthalate aqueous solution was adsorbed on O-cellulose beads for 2 h. The Cu\(^{2+}\)/phthalate-loaded O-cellulose beads were treated with 2 M HCl (8 mL) under stirring of 250 rpm at 25°C for 30 min to desorb the Cu\(^{2+}\)/phthalate from the O-cellulose beads. The re-adsorption test was performed using the HCl-treated O-cellulose beads after complete washing with water at the same conditions as the first adsorption. The adsorption amount of the Cu\(^{2+}\)/phthalate was measured again. The same adsorption and desorption tests were repeated for several cycles. Fig. 7c and d show the adsorption capacity and efficiency of O-cellulose as a function of the number of cycles during the adsorption/desorption of Cu\(^{2+}\)/phthalate, respectively. The efficiency is the relative amount of the adsorption of Cu\(^{2+}\)/phthalate at the \(i\)th cycle compared to that at the \((i-1)\)th cycle defined by equation (11). The adsorption capacity continuously decreases as the number of cycles increases, although the efficiency is constant at ~88%, indicating that the recovery of the oxime groups is high enough for reuse. However, efficiency can be improved by optimizing the desorption conditions.

\[
\text{Efficiency at the } i^{\text{th}} \text{ cycle} = \frac{\text{adsorption capacity at the } i^{\text{th}} \text{ cycle}}{\text{adsorption capacity at the } (i-1)^{\text{th}} \text{ cycle}} \times 100
\]
Fig. 7. (a) Adsorption capacity \( q_t \) of O-cellulose beads made from cellulose (S-S), (S-M), (M-S), and (M-M) beads 40 h after O-cellulose beads (4 mg) were inserted into the vials containing the Cu\(^{2+}\)/phthalate complex (1000 ppm, 4 mL). (b) Reduction of the Cu\(^{2+}\)/phthalate complex aqueous solution (initial concentration; 500 ppm) concentration as a function of the cycle number by passing the complex solution (4 mL) through a column (diameter 5.6 mm) filled with O-cellulose beads (70 mg), with a flow rate of 2.5 mL h\(^{-1}\). The Cu\(^{2+}\)/phthalate complex aqueous solution was circulated for cycling using a syringe pump. (c) Adsorption capacity \( q_t \) and (d) efficiency of O-cellulose as a function of the number of cycles during the adsorption/desorption of Cu\(^{2+}\)/phthalate. The efficiency is the relative adsorption of Cu\(^{2+}\)/phthalate at the \( i \text{th} \) cycle compared to that at the \((i - 1)\text{th}\) cycle defined by equation (11).

**Conclusions**

Uniformly-sized cellulose beads were successfully prepared by coagulating the cell/NMMO droplets that were produced using a microfluidic method with molten state cell/NMMO as a cellulose solvent. The state (solid or molten) of the cell/NMMO droplet and coagulation temperature can control the morphology of the cellulose beads. Coagulation of the molten state cell/NMMO droplet at high temperature (\( \geq 60^\circ\text{C} \)) and amidoxime functionalization could prepare the highly-porous spherical O-cellulose beads with a uniform fibrous open internal structure. The prepared O-cellulose beads showed excellent metal adsorption properties with a maximum adsorption capacity of 80 mg g\(^{-1}\) in the case of Cu\(^{2+}\)/phthalate ions. The novel cellulose beads could be successfully applied to fillers in the column for removing hazardous metal ions.
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Conflict of interest

The authors declare no conflict of interest.

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