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Cationic cellulose hydrogels cross-linked by poly(ethylene glycol): Preparation, molecular dynamics, and adsorption of anionic dyes

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ABSTRACT

Cationic cellulose hydrogels (CCGs) were prepared from quaternized celluloses with degrees of substitution (DS) of 0.56, 0.84, and 1.33, by the cross-linking reaction with poly(ethylene glycol) diglycidyl ether as a cross-linker. The CCGs exhibited swelling behavior in aqueous solutions, which was not affected by pH and temperature of the solution because of the presence of quaternary ammonium groups in their structures. The CCGs showed adsorption ability toward anionic dyes in aqueous solution, which increased with increasing DS. The dye adsorption was found to follow the pseudo-second order kinetic model and the equilibrium isotherm data can be described by the Langmuir adsorption model. In addition, the CCGs could be regenerated and proved to be recyclable adsorbents for wastewater treatment.

1. Introduction

The presence of dyes in wastewater is an important environmental problem because of their high visibility, resistance, and toxic impact (Pushpa et al., 2015). Even very low concentrations of dye can reduce the photosynthetic activity in aquatic environments by preventing the penetration of light and oxygen (Khatri, Peerzada, Mohsin, & White, 2015). Because of their complex aromatic structures, dyes are non-biodegradable substances that are stable under various conditions; they have direct and indirect toxic effects on humans and are associated with diseases such as cancer, tumors, and skin irritation (Vakili et al., 2014).

Various treatment methods have been investigated for the removal of dyes from wastewaters, e.g., coagulation/flocculation (Verma, Dash, & Bhunia, 2012), chemical precipitation (Pan, Wang, Sun, Liu, & Zhang, 2016), reverse osmosis (Zheng, Wang, & Wang, 2015), and membrane filtration (Guo, Zhang, Cai, & Zhao, 2016). However, these methods have several limitations, including high capital and operating costs and low removal efficiency. Adsorption is one of the preferred techniques because it is relatively rapid, convenient, and easy to perform (Yagub, Sen, Afroze, & Ang, 2014; Mu & Wang, 2016).

The adsorption efficiency is generally affected by the nature of the adsorbent. Many adsorbents, such as activated carbon, zeolites, silica gel, and alumina, have been tested for their potential to lower dye concentrations in aqueous solutions. However, despite their relatively low cost, their wider use is restricted by the difficult recycling (Yagub et al., 2014). An ideal adsorbent for dye removal should have properties such as ease of regeneration, environmental safety, low-cost productivity, and high adsorption capacity. Hence, recently, attention has been directed toward natural polysaccharide-based hydrogels because of their biocompatibility and biodegradability (Crini, 2006).

Cellulose, the most abundant natural polymer on earth, is one of the most environmentally friendly non-food sources for the production of a wide range of eco-friendly products. The numerous potential chemical modifications of cellulose also make it an attractive adsorbent hydrogel candidate. For example, the hydrogel prepared from sodium carboxymethyl cellulose, which is a water-soluble anionic cellulose derivative, has shown promising results as adsorbent for cationic compounds (Zhang, Yi, Deng, & Sun, 2014), whereas a quaternary ammonium sodium salt derivative of cellulose, prepared by the homogeneous reaction of cellulose with 2,3-epoxypropyl trimethyl ammonium chloride (EPTMAC), proved effective for anionic compounds (Quinlan, Tanvir, & Tam, 2015). Quaternized cellulose derivatives are advantageous for biomedical, pharmaceutical, and environmental applications because their tertiary ammonium groups exhibit intermediate basicity and are permanently charged regardless of the pH of the solution (Saini,

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Falco, Belgacem, & Bras, 2016). In addition, they are reported to be excellent flocculants for kaolin suspensions because of the charge neutralization between the negatively charged surface of kaolin particles and the cationic groups of quaternized cellulose (Yan, Tao, & Bangal, 2009). Thus, quaternized cellulose is expected to be a powerful candidate for forming the matrix of hydrogels for cationic dye adsorption.

Polyethylene glycol (PEG), which is a synthetic polymer that is amphiphilic (Bailey & Koleske, 1991, 1976) and nontoxic, can be frequently used as an excipient or as a carrier in different pharmaceutical formulations, foods, and cosmetics (Fuertges, & Abuchowski, 1990). PEGs are readily available in a range of molecular weights (Mw); most of those that have low Mw (<10^4) can be rapidly removed from the human body after consumption (Working, Newman, Johnson, & Cornacoff, 1997), making them widely used for biomedical research, drug delivery, tissue engineering, and surface functionalization of biomaterials (Craig, 2002; Torchilin, 2002). The wide range of available PEGs with functionalized end-groups (e.g., azides, thiols, carboxylic acids, hydroxyls, and epoxides) makes them increasingly attractive for use in biomedical and biomaterial research (Zalipsky, 1995). In particular, poly(ethylene glycol) diglycidyl ethers (PEGDEs) which are epoxy-functionalized PEGs are well known for their reactivity toward hydroxyl groups, and are thus used to polysaccharides to form the ether crosslinkage (Cesteros, Ramírez, Peciña, & Katime, 2006; Nielsen, Wintgens, Larsen, & Amiel, 2009).

In this study, a series of cationic cellulose hydrogels (CCGs) with different degree of substitution (DS) were prepared from quaternized cellulose by use of PEGDE as a crosslinking agent (Fig. 1) and their adsorption capacity towards three kinds of anionic dyes, namely, AR13, AB92, and AR112 (Fig. S1), was investigated. In addition, the effect of the DS and pH on the adsorption of anionic dyes on the hydrogels, and the kinetics and isotherms of the adsorption process were evaluated and compared in detail for the elucidation of the adsorption mechanism. Moreover, the recycling efficiency of the adsorbents was determined.

2. Experimental

2.1. Materials

Powdered cellulose with an average polymerization degree of 320 was obtained from Wako Pure Chemicals Industries (Japan). EPTMAC and PEGDE with an average polymerization degree of 7.2 (Kono, Nakamura, Hashimoto, & Shimizu, 2015) were purchased from Sigma-Aldrich Inc. (USA). AR13, AB92, and AR112 were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Other chemicals were of chemically pure grade and all solutions were prepared with pure water.

2.2. Preparation of CCs 1–3

A series of CCs (**1–3**) were prepared following a previously reported method, using an organic synthesizer Process Station PPS-2511 (Tokyo Rikakikai. Co., Ltd., Japan) equipped with a precise temperature control unit and a Teflon stirring impeller (Yan et al., 2009; Kono & Kusumoto, 2015). Briefly, 1.26 g of cellulose (7.78 mmol of anhydroglucose unit (AGU)) was suspended in 50 mL of 1.5 mol L^{-1} NaOH solution containing 1 g of urea, and the suspension was cooled to 259 K. After 1 h, the temperature was controlled at 271 K and the suspension was vigorously stirred at 800 rpm for 10 min to completely dissolve the cellulose. EPTMAC (8.89 g, 58.6 mmol) was added dropwise over a period of 10 min and the reaction mixture was heated at 333 K for 3 h. After cooling to room temperature, the mixture was poured into 300 mL of methanol. The obtained precipitates were washed with a 1:1 mixture of methanol/distilled water to reach a neutral pH, and dried under vacuum to obtain CC **1**. CC **2** was prepared similarly but using an increased amount of EPTMAC (11.8 g, 77.8 mmol). CC **3** was prepared by performing twice the preparation procedure of CC **2** (Table S1). The obtained CCs **1**–**3** were stored in a desiccator under vacuum.

Table 1
Initial feed amounts of each CC and PEGDE used in the synthesis of CCGs **1**–**3** and the corresponding yields.

CCG	Initial feed amount in g (mmol)				CR[b]	Yield in g (mol%)[c]
	CC **1**	CC **2**	CC **3**	PEGDE		
1	5.0 (22)[a]			2.9 (9.2)	0.20	6.2 (89)
2		5.0 (19)[a]		2.9 (9.2)	0.22	6.0 (87)
3			5.0 (16)[a]	2.9 (9.2)	0.23	5.7 (87)

[a] Molar feed amounts of each CC were calculated based on AGU.
[b] Number of PEGDE cross-linked with each CC per AGU.
[c] Yield of each CCG was determined based on the AGU.

2.3. Preparation of CCGs 1–3

CCGs **1**–**3** were prepared from CCs **1**–**3**, respectively, by the following method. The CC (5.0 g) was completely dissolved in 25 mL of a 1.5 mol L^{-1} NaOH solution at 277 K and the solution was stirred at 300 rpm with a Teflon impeller. PEGDE (2.9 mL, 9.16 mmol) was added and the cross-linking reaction was performed at 333 K for 3 h with continuous stirring. The mixture was added to 100 mL of methanol to precipitate the gel. The gel was washed three times with a 1:1 mixture of methanol/distilled water and then precipitated with methanol. The precipitate was dried under reduced pressure at 298 K. The resultant solid particles were cut and screened through a 20 mesh filter using a PLC-2M plastic cutting mill (Osaka Chemical Co., Japan) to obtain the CCG as a white granular solid (Table 1).

2.4. NMR spectroscopy

All NMR spectra were obtained using a Bruker AVIII500 spectrometer (Bruker BioSpin GmbH, Germany). Solution-state ^{13}C NMR spectra were obtained in deuterium oxide at 298 K using a two-channel 5 mm broadband observe probe with a *z*-gradient coil, employing inverse-gated ^{1}H decoupling technique, as previously reported for the quantitative analysis (Kono & Kusumoto, 2015). The chemical shifts were calibrated by assigning the value of 0 ppm to the methyl signal of the internal standard 4,4-dimethyl-4-silapentane-1-sulfonic acid.

Solid-state ^{13}C NMR spectra were recorded at 298 K with a 4 mm dual-tuned MAS probe at 8–10 kHz. For the cross-polarization/magic-angle spinning (CP/MAS) ^{13}C NMR measurements, the contact time, acquisition time, and repetition time were set at 2 ms, 15 ms, and 4 s, respectively. The dipolar-decoupled magic angle spinning (DDMAS) ^{13}C NMR spectra were recorded by setting the ^{13}C excitation pulse length (flip angle of 30°), data acquisition time, and repetition time at 1.35 μs, 15 ms, and 30 s, respectively. The chemical shifts were calibrated by assigning the value of 176.03 ppm to the carbonyl carbon of the external standard D-glycine.

The solid $T_{1\rho H}$ and T_{1C} measurements were performed according to the methods previously reported (Kono et al., 2015). For the $T_{1\rho H}$ measurement, ^{13}C CP/MAS spectra were recorded by inserting variable delays of 0.1, 0.2, 0.5, 1, 2, 3, 5, 10, 15, and 20 ms prior to CP, and the $T_{1\rho H}$ values for the specific ^{13}C resonance regions