



Carboxymethylated cellulose nanofibrils (CMCNFs) embedded in polyurethane foam as a modular adsorbent of heavy metal ions

Hye-Jin Hong^{a,1}, Jin Seong Lim^{b,1}, Jun Yeon Hwang^b, Mikyung Kim^c, Hyeon Su Jeong^{b,*},
Min Sang Park^{d,*}

^a Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon, 34132, Republic of Korea

^b Institute of Advanced Composite Materials, Korea Institute of Science and Technology, 92 Chudong-ro, Bondong-eup, Wanju-gun, Jeonbuk, 565-905, Republic of Korea

^c Seoul Centre, Korea Basic Science Institute, Seoul, 02841, Republic of Korea

^d Global Technology, SK Innovation, 325, Exporo, Yuseong-gu, Daejeon, 34124, Republic of Korea

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ABSTRACT

Polyurethane (PU) foam was utilized as an efficient and durable template to immobilize surface-functionalized nanocellulose, carboxymethylated cellulose nanofibrils (CMCNFs), to address some of the challenges for the application of nanocellulose to industrial water purification, such as its agglomeration, difficulties in separation from effluent, and regeneration. The composite foams exhibited well dispersed CMCNFs in PU matrices with open pore structure; the hydrogen bonds result in the enhancement of mechanical strength, which is another requirement of ideal adsorbents for wastewater treatment. The composite foams show high adsorption capacity and the potential for recyclability. The combination of optimal surface modification of nanocellulose with isolation and immobilization in durable PU foam achieved an efficient and cost-competitive bio-sorbent for heavy metal ions.

1. Introduction

Bio-sorption for wastewater treatment has received much attention due to its ability to capture dissolved metals from dilute solutions with high efficiency, rapid intrinsic kinetics (Volesky, 2007; Wang & Chen, 2009) and cost compatibility (Bailey, Olin, Bricka, & Adrian, 1999). Recently, numerous approaches have been studied for the development of biological materials with high metal-binding capacity and high selectivity (Veglio & Beolchini, 1997; Wang & Chen, 2009). Among these, cellulose and its derivatives, which are abundant in nature and are renewable, represent an attractive bio-sorbent because of their easy chemical modification (Crini, 2005; Habibi, 2014; O'Connell, Birkinshaw, & O'Dwyer, 2008), chemical stability (Crini, 2005), and hydrophilicity in order to reduce bio-fouling or organic fouling (Mansouri, Harrisson, & Chen, 2010) that results from the presence of functional moieties such as hydroxyl, amino, and acetyl groups in polymer chains.

Nanocellulose is a particularly efficient adsorbent because the nano-dimension in size significantly enhances the specific areas associated with sorption sites and shortens the intra-particle diffusion distance resulting in fast kinetics (Qu, Alvarez, & Li, 2013; Sehaqui, Zhou,

Ikkala, & Berglund, 2011; Voisin, Bergström, Liu, & Mathew, 2017). In addition, there have been significant advances in a wide range of facile processes that produce cellulose in the nano-fibrillar (Isogai, Saito, & Fukuzumi, 2011; Peng, Gardner, & Han, 2012) or nano-whisker form (Brinchi, Cotana, Fortunati, & Kenny, 2013; Reid, Villalobos, & Cranston, 2017). Surface chemical modifications of nanocellulose produce significant increase in interaction with contaminants like metal ions (Singh, Arora, Sinha, & Srivastava, 2014; Yao, Wang, Cai, & Wang, 2016; Yu et al., 2013), dyes (Batmaz et al., 2014; Jin, Li, Xu, & Sun, 2015), organic liquids (Wang et al., 2014; Zhang, Sèbe, Rentsch, Zimmermann, & Tingaut, 2014), and microbes (Lin & Dufresne, 2014) in aqueous medium. Therefore, nanocellulose, which offers a combination of bio-sorption properties arising from the unique cellulose nature and nano-dimension, has an obvious potential for a new and green route to develop current water purification technology.

However, some challenges for applying nanocellulose to the water purification industry still exist, which are related to its agglomeration and difficulties in the separation from the effluent (Park, Yun, & Park, 2010; Vijayaraghavan & Yun, 2008). One of the practical approaches to address these issues is to embed nanocellulose in a polymer matrix, in a manner that allows the adsorbents to interact freely with the pollutants

* Corresponding authors.

E-mail addresses: jeonghs98@kist.re.kr (H.S. Jeong), azopark@gmail.com (M.S. Park).

¹ Co-first authors.

and be easily separated from polluted water (Mahfoudhi & Boufi, 2017). Indispensable requirements of such a polymer matrix include its high mechanical strength and stability under different environmental conditions. In addition, the appropriate morphology exhibiting porous structure with high surface area is sought for high accessibility of pollutants into the embedded adsorbents. Polyurethane (PU) foam can satisfy these requirements, and has thus been utilized as a matrix material for immobilizing various adsorbents like activated carbons (Li & Liu, 2012), biomass (Zhou, Li, Bai, & Zhao, 2009), clays (Unuabonah & Taubert, 2014), and hydroxyapatite (Jang, Min, Jeong, Lyoo, & Lee, 2008). However, there have been very few efforts to embed nanocellulose into PU foam for removing heavy metal ions in aqueous solution.

In the present study, we investigated carboxymethylated cellulose nanofibrils (CMCNFs) as a metal-binding adsorbent and fabricated a series of CMCNF embedded PU composite foams. The structural characteristics and mechanical properties of the composite foams were analyzed based on the relevance of the adsorbent. Adsorption performance for the divalent metal ions (Cu^{2+} , Cd^{2+} , and Pb^{2+}) was investigated along with the evaluation of recyclability. The results demonstrate that nanocellulose embedded PU foams have high potential as a modular adsorbent of heavy metal ions.

2. Materials and methods

2.1. Materials

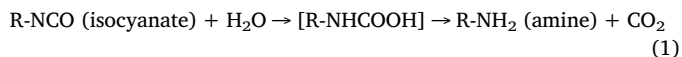
The waterborne PU prepolymer (HYPOL™ JT6000) was purchased from DOW Chemicals. HYPOL™ JT6000 is a NCO-terminated hydrophilic toluene-diisocyanate (TDI)-based polyurethane prepolymer suitable for use in two-component formulations, mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate. HYPOL™ JT6000 react with other components containing isocyanate reactive moieties such as hydroxyl, amine, carboxyl functional groups, rendering hydrophilic PU polymer. Most commonly, the reactive component is an aqueous phase and hydrophilic foam of different cellular structure can be obtained according to the ratio of PU prepolymer to aqueous phase. No catalyst is required during the reaction. Viscous CMCNF solution in DI water (3 wt %) was provided by Asia Nanocellulose and diluted with DI water to use as an adsorbent filler solution. Because there are only few information about CMCNF that could be provide from supplier, we analyzed CMCNF which we used and described its characteristics such as degree of substitution (DS) of carboxymethyl group, diameter and morphology in detail at Section 3.1. Copper sulfate (CuSO_4 , Wako), cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Junsei) and lead nitrate ($\text{Pb}(\text{NO}_3)_2$, Samchun) were used as heavy metal reagents. To control the initial pH of the solution, 0.1 M HCl (Junsei) and 1 M NaOH (Junsei) were used.

2.2. Preparation of PU composite foams

To produce waterborne PU, an amount of 30 g of deionized (DI) water was vigorously mixed with 10 g of prepolymer using a mechanical stirrer for 30 s at room temperature. In case of CMCNF embedded PU composite, CMCNF suspension in DI water was prepared and mixed with PU prepolymer. The loading contents of CMCNF in the filler solution were controlled by adjusting the amount of water to the as-received CMCNF solution (3 wt%). The details are listed in Table S1 (Supporting Information). We note that the maximum loading amount of CMCNF to the amount of PU in the composite was limited to 4 wt% because the viscosity of filler solution became too high to carry out mixing.

The mixed solution was poured into a rectangular tray (schematic draw in Fig. S1). A foam structure was developed simultaneously due to the release of CO_2 gas from the reaction between isocyanate (R-NCO) in the prepolymer and water (H_2O). After reaction of PU prepolymer with H_2O , isocyanate (N–C–O) group completely converts to amine like

chemical Eq. (1).



Thus, as the water was consumed in the formation of CO_2 bubbles, the CMCNFs were naturally attached onto the surface of PU foam, following 3D porous foam structures.

After drying for 10 min at room temperature, the composite foam obtained from the tray was washed several times with DI water and dried overnight at 60 °C. The PU/CMCNF composite was then cut into rectangular shaped pieces (2 cm (width) by 2 cm (length), weight 0.3 g) for the adsorption experiment.

2.3. Characterization methods

Transmission electron microscopy (TEM, Tecnai F20, FEI) and scanning electron microscopy (SEM, Verios 460L, FEI) equipped with energy dispersive X-ray spectroscopy (EDS) were used to observe the morphology of CMCNF and PU/CMCNF composite foams, respectively. The internal 3D structure of the composite foam was determined by non-destructive x-ray microscopy (XRM, Xradia 520 versa, Zeiss, Germany), and the obtained XRM image was further analyzed by 3D software (Avizo Fire 8.1, FEI). The chemical structure was investigated by Fourier-transform infrared spectroscopy (FT-IR, Cary 630, Agilent, USA). The surface charge of CMCNF was investigated by measuring the zeta-potential using a Zetasizer system (Nano ZS, Marvern, UK). The mechanical properties of the composite foams were tested in the tensile mode using a universal testing machine (5567A, Instron, USA).

2.4. Evaluation of adsorption performance

A piece of the PU/CMCNF foam was placed in 50 mL of heavy metal solution to evaluate the adsorption performance. Before adsorption, the solution pH was maintained at 5.0 to prevent precipitation of the heavy metals. The mixture was stirred with an end-over shaker for 24 h. After the adsorption process, the solution was filtered through a syringe filter of pore size 0.2 μm and the heavy metal concentration was quantified.

The maximum absorption efficiency was obtained with PU/CMCNF-4 and the values for Cu^{2+} , Cd^{2+} , and Pb^{2+} were 40%, 61%, and 95%, respectively. The adsorption capacity q_e (mg/g) of the CMCNFs embedded in the PU foam was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 (mg/L) is the initial metal ion concentration, C_e (mg/L) is the metal ion equilibrium concentration, V (L) is the volume of the metal ion solution, and m (g) is the mass of CMCNF embedded in PU foam.

For the regeneration, the heavy metals adsorbed on the PU/CMCNF were reacted with 0.1 M HCl for 6 h and washed several times with DI water. The regenerated PU/CMCNF composite was dried at 60 °C in an oven to remove the moisture. The concentration of heavy metals was analyzed by Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin-Elmer, USA).

3. Results and discussion

3.1. Characterization of carboxymethylated cellulose nanofibril (CMCNF)

Carboxymethylated cellulose nanofibril (CMCNF) has carboxymethyl groups ($-\text{CH}_2-\text{COONa}$) bound to the CNF backbone. In general, the substitution of polar carboxymethyl groups renders CNF soluble (Kargl et al., 2012) and the solubility depends on the degree of substitution (DS), the number of carboxymethyl groups attached per anhydroglucose unit (Almlöf, Schenzel, & Germgård, 2013). In this study, the DS of CMCNF was 0.45–0.5 exhibiting both the dissolved form and the dispersed fibrous form in aqueous state. The TEM images

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