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Development of waste biomass based sorbent for removal of cyanotoxin microcystin-LR from aqueous phases

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ABSTRACT

The purpose of this study was to establish the strategy to remove the cyanotoxin microcystin-LR (MC-LR) from aqueous solution with the use of biosorption strategy. Specifically, we focused on use of industrial waste biomass, *Escherichia coli*, to make efficient biosorbents for MC-LR through immobilization of the biomass with polysulfone (PS), coating the polysulfone-biomass composite with polyethylenimine (PEI), and decarboxylation of the PEI-coated composite to remove the inhibitory sites. The resulting sorbent is named in this study as decarboxylated PEI-coated polysulfone-biomass composite fiber (DC-PEI-PSBF). Various sorption experiments including isotherm, kinetics and pH effect on sorption capacity were conducted to evaluate the MC-LR adsorption performance of sorbents. As a result, the DC-PEI-PSBF could be suggested as a highly efficient sorbent able to be directly applied for MC-LR removal from aquatic natures.

1. Introduction

In recent years, frequency and degree of harmful algal blooms (HABs) occurring have increased in precious water resources such as lakes and rivers due to eutrophication of water bodies (Pavagadhi et al., 2013). During widespread occurrence of HABs, various micro-pollutants including cyanotoxins are also discharged indispensably into water resources (Wei et al., 2017). Among cyanotoxins, microcystins (MCs) have been recognized as one of the typical micro-pollutants that have acute toxicity by inhibition of protein phosphatase-1 and -2A, leading to liver damage and tumor growth (Wang et al., 2015). MCs (monocyclic heptapeptides) consisting of seven amino acids, are usually produced from cyanobacteria including *Microcystis*, *Oscillatoria*, *Nostoc* and *Anabaena* species (Dawson, 1998; Hilborn et al., 2005). MCs are biosynthesized from intra-cellular of cyanobacteria species, and released into open waters during biological cell lysis and cell destruction (Pietsch et al., 2002).

In the group of identified molecular MCs variants (above 150 types), microcystin-LR (MC-LR) have been recognized as one of the most commonly detected and most toxic type of MCs (Falconer, 2005; Wei et al., 2017). Due to the threat of MCs, WHO (World Health Organization) recommends 1.0 μg/L of MC-LR as a provisional safety guideline (Li et al., 2017) for the drinking water. Because of its cyclic structure, MC-LR is exceedingly stable and difficult to eliminate from aqueous phases by traditional water treatment technologies (Gao et al., 2016; Lawton and Robertson, 1999; Teng et al., 2013b).

Recently, adsorption technology has attracted increasing interest as a strategy for MC-LR removal because of its suppleness, high removal efficiency and cost benefits (Kim et al., 2016c). Various sorbents including activated carbon (Donati et al., 1994), graphene oxide (Pavagadhi et al., 2013), mesoporous silica (Teng et al., 2013b), and mesoporous carbon (Teng et al., 2013a) were investigated for adsorptive MC-LR removal from aqueous phases. According to Pavagadhi et al. (2013), the maximum MC-LR adsorption capacity (q_m) of the graphene oxide was estimated as 1700 μg/g at pH 5. The wood-based activated carbons showed 20–280 μg/mg of maximum MC-LR adsorption capacity in the Milli-Q water (pH 5.2–6.6) (Donati et al., 1994). In case of the mesoporous silica (SBA-15), the maximum MC-LR sorption capacities were estimated as 4.80 and 5.99 mg/g at 10 and 25 °C in Milli-Q water, respectively (Teng et al., 2013b). Although activated carbon based sorbents revealed potential as an effective adsorbent for MC-LR, it has a limitation due to relatively high operation costs and low energy-efficiency for regeneration of activated carbon after use (Kim et al., 2016c; Sathishkumar et al., 2010). Therefore, attention has shifted to development of biological methods such as biosorption (Vijayaraghavan and Yun, 2008). Various biomaterials including bacteria, fungi, algae, and agricultural/industrial bio-wastes have been applied as biosorbents for the removal of ionic pollutants, heavy metals

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and precious metals, since biomaterials have various functional groups which can be negatively or positively charged including carboxyl, amine, hydroxyl and sulfonate groups as electrostatic attractive binding sites for anionic and cationic materials (Kim et al., 2016c, Volesky, 2007). As a biosorbent, the peat has been applied in adsorption of MC-LR and displayed the maximum MC-LR sorption capacity as 255.71 μg/g at pH 3 (Sathishkumar et al., 2010).

A large amount of biomass wastes including *Escherichia coli* is generated from the industrial scale fermentation process for amino acid production. It has been reported that *E. coli* biomass possesses amine, carboxyl, and phosphonate groups on their surface as main binding sites. Especially, since the possessed amine groups in *E. coli* biomass can be positively charged, it is recognized as main binding sites which can remove anionic pollutants by electrostatic interaction (Kim et al., 2015). In addition, it has been reported that MC-LR can be negatively charged above pH 2.19 by deprotonation of carboxyl groups in MC-LR molecule (Sathishkumar et al., 2010). Therefore, *E. coli* biomass can be potentially recyclable biosorbent for removal of MC-LR from aqueous phases. However, most of this waste biomass is treated by sea dumping, landfill, and incineration. In this study, the main purpose is to fabricate industrial waste biomass as a highly stable and highly efficient adsorbent for MC-LR removal from aqueous solution. To fabricate as a stable adsorbent, *E. coli* biomass was immobilized with polysulfone (PS) matrix to render it with high mechanical and chemical stability. To enhance adsorption performance of waste biomass-based sorbent, PEI-coating providing of numerous main binding sites (amine groups) for MC-LR and additional chemical modification were carried out. In addition, the MC-LR sorption performances of prepared sorbents were thoroughly compared.

2. Materials and methods

2.1. Materials

The waste biomass, *E. coli* was obtained as spray dried from industrial amino acid, L-phenylalanine fermentation process, Daesang Co. (Gunsan, Korea). Polysulfone (PS, $[OC_6H_4OC_6H_4SO_2C_6H_4]_n$, average Mn ~ 22,000 by MO, beads) and branched polyethylenimine (PEI, 50% in H_2O, M.W. ~ 750,000) were purchased from Sigma Aldrich Co., Ltd. *N,N*-dimethylformamide (DMF, C_3H_7NO, 99.8%) and glutaraldehyde (GA, $C_5H_8O_2$, 25 wt%) were supplied from Daejung Chemical & Metals Co., Ltd. (Siheung, Korea) and Junsei Chemical Co., Ltd. (Tokyo, Japan), respectively. The target cyanotoxin, microcystin-LR (MC-LR, isolated from *Microcystis aeruginosa*, > 95%) was purchased from Enzo Life Sciences, Inc. (New York, USA). Trifluoroacetic acid (CF_3COOH, TFA, > 99.5%) was purchased from Alfa Aesar (Thermo Fisher Scientific Inc.). Methyl alcohol (CH_3OH, 99.9%, HPLC grade) and acetonitrile (CH_3CN, 99.9%, HPLC grade) were obtained from TEDIA. All other chemical reagents were analytical grade.

2.2. Preparation of waste biomass based sorbents

To fabricate pristine PS fiber (PSF), the 9%w/v of PS solution was prepared by dissolving PS in DMF and stirring overnight at room temperature. In addition, to fabricate the polysulfone-*E. coli* biomass composite fibers (PSBF), 22.2 g of the *E. coli* biomass was suspended into the 200 g of 9%w/v PS solution for preparation of 10%w/w biomass containing PS-biomass mixture. Subsequently, it was stirred for 10 h at room temperature for uniform dispersion of biomass in the PS-biomass composite solution. Then, these solutions were extruded into deionized water through a plastic hub needle (TAEHA Co., Namyangju, Korea) to form PSF and PSBF. Prepared fibers were washed several times with distilled water to remove residual DMF.

For the PEI-coating on PSBF, PEI was immobilized on the surface of PSBF through the agitating 100 g_{wet} of prepared PSBF into 1 L of 23 g/L PEI solution for six hours. After that, the PEI-immobilized PSBF was washed one time using distilled water to remove residual PEI. Then, cross-linking was allowed using GA. For the cross-linking, PEI-immobilized PSBF was agitated into the 1 L of GA solution (0.7 mL/L) at pH 10.32 for four hours at room temperature. After cross-linking step, PEI-coated PSBF (PEI-PSBF) were separated from the solution and washed three times with deionized water. The prepared fibers were freeze dried for 24 h.

To fabricate the decarboxylated PEI-PSBF (DC-PEI-PSBF), the carboxyl groups on the PEI-PSF was modified by esterification reaction. Two grams of dried PEI-PSBF was suspended in 200 mL of methanol, and 8.6 mL of concentrated hydrochloric acid (HCl, 35%) was added to the suspension. The mixture was stirred for 6 h at 25 °C. After completion of the esterification, DC-PEI-PSBF was separated by filtration, and then washed three times using deionized water. The esterification reaction processed for DC-PEI-PSBF can be represented as follow.

$$\text{Biomass}-\text{COOH} + \text{CH}_3\text{OH} \xrightarrow{\text{H}^+} \text{Biomass}-\text{COOCH}_3 + \text{H}_2\text{O} \quad (1)$$

2.3. Determination of functional groups characteristics on sorbents

Characteristics regarding the functional groups of *E. coli* biomass, PSF, PSBF, PEI-PSBF, and DC-PEI-PSBF were determined using Fourier transform infrared spectrometer (FT-IR, Agilent Cary 630 FTIR, Agilent Technology, USA). These samples were prepared as KBr pallet. Their FT-IR spectra were recorded within the range of 700–4000 cm^{-1}.

2.4. X-ray photoelectron spectroscopy (XPS) analysis

The surface of the PSF, PSBF, PEI-PSBF, and DC-PEI-PSBF were analyzed by XPS (Micro-XPS) to determine the change of elements signal (C_{1s}, O_{1s}, and N_{1s}) related the functional groups in the sorbents. The XPS instrument was calibrated at the Au $4f_{7/2}$ peak (binding energy: 84.0 eV). The X-ray source was operated at 180 W. During XPS measurement, the pressure in the analysis chamber was maintained at less than 7×10^{-9} torr. To determine main element peaks of the sorbents, all binding energies were referenced by the neutral C_{1s} peak at 284.6 eV.

2.5. Adsorption experiments

To evaluate MC-LR sorption performances of prepared sorbents, adsorption experiments were conducted in a batch system. For adsorption experiments, 1000 mg/L of MC-LR stock solution was prepared by dissolving 1 mg of MC-LR standard in 1 mL of methanol. To prepare the MC-LR solution of sorption experiments, the MC-LR stock solution was diluted with deionized water to be desired MC-LR concentrations. To determine the pH effect for MC-LR adsorption capacity of sorbents, MC-LR adsorption was conducted in different pH (pH edge experiment). Particularly, 0.01 g of *E. coli*, PSBF, PEI-PSBF, and DC-PEI-PSBF were suspended in 20 mL of MC-LR solution (initial concentration: 1000 μg/L) and stirred at 190 rpm and 25 °C for 24 h in a shaking incubator. In the case of isotherm experiment, 0.01 g of PEI-PSBF and DC-PEI-PSBF were soaked into 30 mL of MC-LR solutions with different initial MC-LR concentration (100, 200, 300, 400, 500, 700, and 1000 μg/L), and stirred for 24 h at the same condition with pH edge experiment. During isotherm experiments, the pH of samples was controlled to pH 5 and pH 7 by using HCl and NaOH solutions. To evaluate the sorption equilibrium time for MC-LR, kinetic tests were conducted at pH 7 and 25 °C until equilibrium states were achieved. 0.06 g of PEI-PSBF and DC-PEI-PSBF were suspended in 200 mL of MC-LR solution (initial concentration: 566.07 μg/L), respectively. Kinetic samples were collected at the predetermined time. The amount of MC-LR adsorbed on the sorbents was estimated using the following equation:

$$q = (V_i C_i - V_f C_f)/M \quad (2)$$