Importance of the coating pH in fabrication of polyethylenimine-coated polysulfone-*Escherichia coli* composite fiber sorbent

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ABSTRACT

In present study, polyethylenimine-coated polysulfone-*Escherichia coli* biomass composite fibers (PEI-PSBFs) were prepared at different PEI-coating pHs. The PEI-coating pH was the critical factor affecting Pd(II) uptake and the optimum pH was around pH 9. The type and amount of functional groups in the biomass and PEI were estimated using potentiometric titration and proton-binding modeling, and these results used to simulate the pH-dependent speciations of their functional groups. As a result, electrostatic interaction between negatively charged biomass and positively charged PEI was estimated to be the largest at pH 9.2, and was closed to the experimentally obtained optimum PEI-coating pH.

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1. Introduction

Treatment of industrial wastewaters containing metal ions has been regarded as a challenge to chemical and environmental engineers due to their non-degradable nature, high toxicity toward humans and ecological environments [1]. In addition to environmental issue, precious metals (Au, Pd, Pt, Rh, etc.) from secondary source like electric-, electronic and chemical industries are also important in terms of reservation of resource due to their limited deposits and increasing demands and prices [2,3]. Numerous techniques for removal and/or recovery of ionic metals were advanced, including chemical precipitation, filtration, ion exchange, reverse osmosis, electrodialysis, adsorption using synthetic or natural materials, etc. [4,5].

Among various techniques developed so far, biosorption technology that involves adsorption using various biomaterials including marine algae, fungal biomass, activated sludge, and microbial biomass as adsorbents has been recognized as a promising method [2]. Biosorption exhibits excellent characteristics such as cost-effectiveness, biocompatibility, little emission of by-product, and operation simplicity [6]. Biosorbents contain several types of functional groups such as carboxyl, hydroxyl, phosphonate and amine groups. The naturally occurring functional groups can be modified by diverse chemical and/or physical methods including pretreatment, addition of binding site, removal of interfering sites, and coating with ionic polymers for enhancement of their sorption capacities [1,7].

Among various modification methods, coating the biomass with polyethylenimine (PEI) has been proved as an efficient modification method especially for enhancement of anionic precious metal uptake, because PEI has a large amount of amine groups (primary, secondary and tertiary) able to bind anionic metals [8,9]. In addition, the PEI-coated polysulfone-*E. coli* biomass composite fiber (PEI-PSBF), developed sorbent in our previous study, showed the significant enhancement of Pt(IV) uptake after PEI-coating [10]. However, the interaction between the biomass and PEI has not been fully understood.

In the present study, the *E. coli* biomass was used as functional group donor for PEI-coating, since the biomass is generated as waste biomass from the full scale fermentation process for L-phenylalanine production. As shown in Scheme 1, it is sug-

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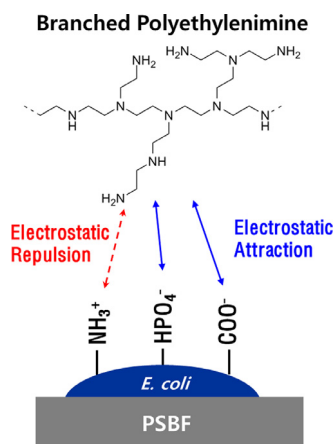
Scheme 1. Conceptual scheme of electrostatic interaction between PEI and the biomass exposed from PSBF.

gested that PEI can be bound to the functional groups of the *E. coli* biomass exposed from the polysulfone-*E. coli* biomass composite fiber (PSBF) by electrostatic attraction. The electrostatic attraction is influenced by the solution pH, because the speciation of functional groups is pH-dependent by deprotonation under the specific pH condition. Therefore, the present study focuses on the effect of pH for PEI-coating on the sorption performance of PSBF. For this, various PEI-PSBFs were prepared at different pHs and compared their sorption capacities of Pd(II), used as a model anionic metal. To estimate electrostatic attraction between PEI and *E. coli* biomass, quantitative analysis of functional groups of the biomass and PEI was carried out by potentiometric titration and proton-binding modeling. Finally, the effect of coating pH on the sorption performance of PEI-PSBF is explained on the basis of the experimental and simulation data.

2. Materials and methods

2.1. Materials

The *E. coli* biomass generated from an L-phenylalanine fermentation company (Daesang, Gunsan, Korea) was obtained as inactivated and dried powder form by acid-treatment and spray-drying process. The inactivated biomass was washed with 1 M HCl solution for one day to remove nutrient salts and to protonate the functional groups on the biomass surface. Polysulfone and 99.8% N,N-dimethylformamide (DMF) were purchased from Sigma-Aldrich Korea, Ltd and Daejung Chemical & Metals Co., Ltd. (Siheung, Korea), respectively. Industrial-grade branched PEI (M.W.: 70,000, content: 50%) was purchased from Habjung Moolsan Co., Ltd. (Seoul, Korea). Palladium(II) chloride (PdCl$_2$, 99.0%) and 25 wt.% glutaraldehyde (GA) were supplied by Kojima Chemicals Co., Ltd. and Junsei Chemical Co. Ltd., respectively. All of the other reagents used in present research were of analytical grades.

2.2. Preparation of polysulfone-based fibers

To manufacture polysulfone-biomass composite fiber (PSBF), 9 % w/v polysulfone solution was prepared by dissolving 9 g of polysulfone in 100 mL of DMF and the resulting solution mixture was stirred for 10 h at 40 °C. The *E. coli* biomass-polysulfone solution (14 % w/v) was prepared by dispersing the protonated *E. coli* biomass in the 9 % w/v polysulfone solution. The mixture was agitated with a mechanical stirrer for 10 h at room temperature. Then, this solution was extruded through a plastic hub needle (TAEHA

Co., Namyangju, Korea) with a 0.3 mm diameter into deionized water to form PSBF. Prepared PSBF (fiber size: 410.48 ± 37.04 μm) was washed several times with distilled water to remove any residual DMF and dried for 24 h using a freeze dryer (TFD Series, Ilshinbio, Korea).

2.3. PEI-coating on the polysulfone-biomass fiber

In 100 mL of 6.9 g/L PEI solution 0.3 g of PSBF was soaked and stirred for 6 h. In the PEI-coating step, the pH of the solutions was controlled to pH 5–11 using 1 M NaOH and 3 M HCl solutions. After that, the PEI-coated fiber was washed once using D.I. water to remove remaining PEI, further cross-linking was carried using 100 mL of 0.63 mL/L GA solution for 4 h at 40 °C. In the cross-linking step, the solution pH was adjusted to around pH 10.3. After the cross-linking reaction, PEI-coated polysulfone-biomass composite fibers (PEI-PSBF) were separated, washed with deionized water several times, and freeze dried for 24 hours.

2.4. Potentiometric titration

Fifty-milliliter polypropylene bottles were used for the titration experiments. To maintain the ionic strength of titration samples, 5 g of biomass or PEI was suspended in 1 L of 0.1 M NaCl solution (CO$_2$-free), and the initial pH was adjusted to pH 2 using 1 M HCl and 1 M NaOH solutions. Twenty-milliliters each, of the biomass and PEI suspensions were filled into the polypropylene bottle and, different volumes of 0.5 M HCl and 0.5 M NaOH solutions (0.1 M NaCl based) were added. The bottles were agitated using a shaker at 160 rpm and room temperature (25 ± 0.2 °C) for over 12 h. Finally, the equilibrium pH was measured using an electrode (Ingold). During the potentiometric titration experiments, CO$_2$-free conditions were maintained through N$_2$ purging to avoid the influence of inorganic carbon on the pH of the solutions. The potentiometric titration was duplicated.

2.5. Adsorption experiment

For the sorption experiments, 1,000 mg/L of Pd(II) stock solution was prepared by dissolving PdCl$_2$ in 0.1 M HCl solution. 0.05 g of the prepared PEI-PSBFs at different pH was suspended in 30 mL of 1000 mg/L Pd(II) solutions, and stirred at 140 rpm and 25 °C in a shaking incubator for 24 h. During the batch experiment, the solution pH was not adjusted, because the pH of the solution was maintained at around pH 1.2 during the sorption process. The sorption experiments were duplicated. After the adsorption process, samples were collected and centrifuged at 10,000 rpm for 5 min. The Pd(II) concentration in the supernatant was measured using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (ICPS-7500, Shimadzu, Japan) after proper dilution. The amount of Pd(II) adsorbed on the fiber sorbents was calculated using the following equation:

$$q = \frac{(C_i - C_f)V}{X} \tag{1}$$

where q is the Pd(II) uptake (mg/g), C$_i$ and C$_f$ (mg/L) are the initial and final concentrations of Pd(II), and V and X indicate the volume (L) of the sample and the weight of fiber sorbents used, respectively.

2.6. FT-IR analyses

FT-IR spectroscopy was used to analyze the functional groups of PSBF and PEI-PSBF. The samples were prepared as KBr discs. Their FT-IR spectra were recorded within the range of 4000–400 cm^{-1} using FT-IR (FT/IR-300E, JASCO, Japan).