산업 발효 폐기물인 Corynebacterium glutamicum 바이오매스를 이용한 수계로부터의 유가금속 회수에 대한 연구

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An advanced approach for recovery precious metal from aqueous solution using industrial fermentation waste biomass of *Corynebacterium glutamicum*

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Introduction

Platinum-group metals (PGM), such as Pt, Rh, Pd, Ir and Ru, are precious metals and are widely used in industries because of their specific physical and chemical properties. Conventional methods for the removal of low concentrations of dissolved metal ions from wastewater include solvent extraction, chemical precipitation and ion exchange. However, these methods have significant disadvantage, such as incomplete metal removal, high capital costs, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal [1, 2]. Many research groups are investigating the possibility of using waste biomaterials for metal uptake [3, 4]. Biosorption technique involves in using materials of biological origin, more specifically living or dead microorganisms, to accumulate solute on the surface of the sorbent. The mechanisms of the biosorption are generally based on physic-chemical interaction between metal ions and the functional groups resent on the cell surface, such as electrostatic interaction, ion exchange and metal ion chelation or complexation [5].

Corynebacterium glutamicum, a gram positive bacterium, is widely used for the biotechnological production of amino acids. Currently, the production of amino acids from fermentative processes using *C. glutamicum* amounts to 1,500,000 and 550,000 t per year of L-glutamate and L-lysine, respectively [6]. Hence the waste biomass *C. glutamicum* generated after fermentation could be potential raw material for biosorbent.

In this study, *C. glutamicum* was evaluated as a biosorbent for the removal of Pt(IV) from the aqueous solution. A series of batch experiments has been carried out.

Materials and method

Materials

All chemicals used in this study except Pt(IV) were of analytical grade and purchased from Sigma-Aldrich Korea Ltd. Platinum solutions were prepared from potassium hexachloroplatinate (IV) (K₂PtCl₆, Kojima Chemicals Co. Ltd., Japan) in hot distilled water.

The *C. glutamicum* biomass was obtained in the form of powder from a MSG fermentation industry (Deasang, Gunsan, Korea). The biomass was prepared by using spray-drying process for 24 h, and subsequently used in biosorption experiments.

Sorption experiments

For biosorption experiments, 0.03 g of biomass was brought into contact with 30 mL of Pt(IV) solution in a 50 mL falcon tube. The pH of solution was initially adjusted to the desired value and controlled using 1 M HCl and 1 M NaOH. The tubes were then kept in an incubated rotary shaker at 160 rpm at $25 \pm 2^{\circ}$ C. After obtaining the equilibrium, the biosorbent was separated by centrifugation at 9000 rpm for 5 min. Effect of contact time was studies as same as the biosorption experiments except that the samples were collected at fixed time intervals.

In this study, the Pt(IV) concentrations in all the samples were analyzed with an Inductively Couple Plasma Spectrometer (ICP-7510, Shimadzu, Japan).

Results and discussion

pH edge

The solution pH affects the speciation of metals and activities of the functional groups on the biomass surface. As shown in Fig. 1, the sorption capacity decreased with pH increasing. Since in acidic conditions, platinum occurs mostly in anionic form while the functional groups on the biomass surface were supposed to be protonated, it appears that binding of this metal is consistent also with electrostatic forces. At low pH values, the overall surface charge on the biomass becomes positive and may assist the interaction with the negatively charged Pt(IV) ions.



Fig. 1. The pH effect on the biosorption of Pt(IV) at $25 \pm 2^{\circ}C$ for 24 h

Isotherms

In order to evaluate the maximum biosorption potential of *C. glutamicum*, isotherm experiments were conducted at pH 2.5 and 5.0, respectively (Fig. 2). The ratio between the Pt(IV) concentration remaining in solution and that sorbed onto the solid decreased with increase in the Pt(IV) concentration, providing a concave curve with a strict plateau. Langmuir model, $Q=Q_mbC_f/(1+bC_f)$, in non-linear form [7], was used to describe the isotherm data. Here, the constant, " Q_m " is often used to compare the performance of biosorbents; while "b" characterizes the initial slope of the isotherm. The maximum Pt(IV) uptake value, 92.78 and 75.25 mg/g, were found at pH 2.5 and 5.0, respectively; whereas, *b* values of 0.055, 0.009 L/mg were shown at pH 2.5 and 5.0, respectively. The correlation coefficient (R^2) values were greater than 0.996.



Fig. 2. Biosorption isotherms of Pt(IV) onto C .glutamicum at temp. $25 \pm 2^{\circ}$ C for 24 h

Effect of contact time

Time needed for the treatment of precious metal wastewater is an important factor from the economical point of view. Fig. 3 shows the Pt(IV) uptake by *C. glutamicum* as a function of time for different initial Pt(IV) concentrations. As a result, the sorption process was found to be very rapid, and the equilibrium of sorption process could be reached within approximately 10 min. the uptake of Pt(IV) increased with the initial platinum concentration because of increase in driving force [8]. Here, it can be noted that a higher initial concentration of Pt(IV) uptake makes the adsorption process faster.



Fig. 3. Removal efficiency of Pt(IV) onto *C. glutamicum* as a function of time for various initial Pt(IV) at pH 2.3 and $25 \pm 2^{\circ}$ C

Desorption

The regeneration of the biosorbent is likely to be a key factor in assessing its potential for commercial application [9]. Pt(IV) was eluted from the Pt(IV)-loaded biomass using 3 kinds of eluents, i.e. 3 M NaOH, 3 M HCl and 0.1 M thiourea dissolved in 0.1 M HCl solution, respectively. As shown in Fig. 4, the Pt(IV)-loaded *C. glutamicum* eluted by 0.1 M thiourea showed highest desorption efficiency (73.9%), and then that of 52.8% with 3 M NaOH. And also it was found that there was no significant desorption efficiency using 3 M HCl.



Fig. 4. Sorption and desorption of C. glutamicum for the Pt(IV) biosorption at $25 \pm 2^{\circ}$ C for 24 h

Conclusions

The present investigation showed that the pH value of the solution is an important controlling parameter in the adsorption process. The removal of Pt(IV) decreased with increasing pH. Langmuir model was employed to fit the experimental data, which was found to be well represented with high correlation coefficient. The maximum Pt(IV) uptake values, Q_m , were 92.78 and 75.25 mg/g at pH 2.5 and 5.0, respectively. Furthermore, a swift biosorption process and facile regeneration make *C. glutamicum* a good biosorbent with great application potential in the future.

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