포스터 발표 P-31

전기화학 막 반응기에서의 고정화 효소를 이용한 아조염료의 분해

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Degradation of Azo Dye in an Electrochemical Membrane Reactor Using an Immobilized Enzyme

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1. Introduction

A multitude of synthetic dyes are used for textile dyeing, paper printing, and colour photography. Azo dyes are an abundant class of synthetic, coloured, organic compounds, which are characterized by the presence of one or more azo bonds (-N=N-). They are produced in quantities that exceed 7×10^5 tons/year[1]. There is significant environmental concern for the decolorization of azo dyes in a wide range of textile and dyestuff wastewater. Traditional techniques for treating dye wastewater are biological treatment, adsorption on activated carbon, and chemical oxidation. They have several drawbacks, such as high operational costs and limited applicability[2].

Horseradish peroxidase (HRP, EC 1.11.1.7) is known to catalyze the oxidation of aqueous aromatic compounds, and efficiently cleave azo compounds in the presence of hydrogen peroxide. The traditional methods for the activation of peroxidase were conducted with an external supply of H_2O_2 for maintenance of enzyme activity in the degradation of pollutants[2,3,4]. This study was focussed on the *in situ* generation of H_2O_2 and its use for enzymatic degradation of azo dye (orange II) in an electrochemical reactor using a cation exchange membrane.

2. Experimental

Horseradish peroxidase, type VI-A (HRP, EC 1.11.1.7), and Celite® R-646 as a support material were purchased from Sigma and Celite Corporation respectively. Other chemicals used in this study were obtained from the Sigma Aldrich Chemical Company (USA) and all solutions were prepared with deionized-distilled water.

The Celite beads were extensively washed by for 1 hr in distilled water, and a 10 % (v/v) aqueous solution of 3-aminopropyl -triethoxysilane adjusted to pH 4 was added. After a 3-h reaction at 70℃, the beads were dried at 110℃ overnight. The beads were thoroughly washed with distilled water and dried at 80℃[5]. The aminopropyl-Celite beads were then immersed in 2 % (v/v) aqueous glutaraldehyde for 2 h with constant agitation at room temperature. The beads were then thoroughly washed and immersed in HRP solution for 5 h at room temperature. The immobilized Celite beads were thoughly washed and ready for use[6].

A two-compartment circular membrane reactor was used in this study. A cation exchange membrane (Nafion 117, Aldrich, USA) was placed between the two compartments to allow proton transport. Two circular plates (d=5cm) of platinum-coated titanium were used as electrodes. HRP immobilized Celite beads were packed into the cathodic compartment. The anolyte was 100 mM phosphate buffer solution (pH 7.0) and certain concentrations of orange II in the same buffer were used for the catholyte. Oxygen gas was supplied into the vessel of catholyte. It was conducted under constant current mode using a DC Power Supply (6613C, Agilent). Fig. 1 shows the experimental set-up used in this study. The analysis of orange II and hydrogen peroxide were carried out with the calibration method. Residual concentration of orange II was determined at λ_{max} = 484 nm by UV-VIS spectrophotometer (UV-1601PC, Shimadzu Co.). The concentration of H_2O_2 was measured at 454 nm according to the DMP method[2]. Sulfanilic acid was measured by ion chromatography (DX120, DIONEX) using a standard anion column.

3. Results and Discussion

The roles of membrane are separating oxdiation-reduction reaction in the

reactor, and selective transport of proton for the H_2O_2 electrogeneration. H_2O_2 is essential for the HRP activation, and it can be generated by the electrochemical reduction of oxygen in the cathode[4]. As shown in Fig. 2, the highest H_2O_2 formation was appeared at 15 Am^{-2}, while the power consumption increased with current. The effects of temperature and pH value were examined for the electrochemical membrane reactor using the immobilized HRP. From Fig. 3, it was found that the highest degradation efficiency of orange II occurred at pH 6~7, and increased with temperature. The electroenzymatic degradation of azo dye in an electrochemical membrane reactor is illustrated in Fig. 4, and it shows time course for disappearance of orange II and appearance of a degradation product, sulfanilic acid which is consistent with reductive cleavage of the azo group. During the operation, the degradation efficiency of azo dye was maintained over 90 %, and the dye color was significantly disappeared.

Acknowledgement

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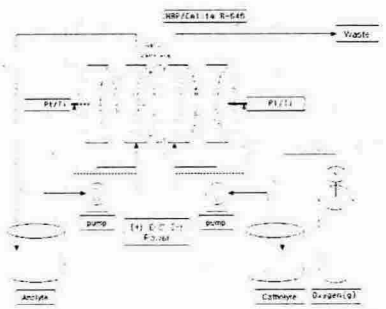

Fig. 1. Schematic diagram of the electro-chemical membrane reactor.

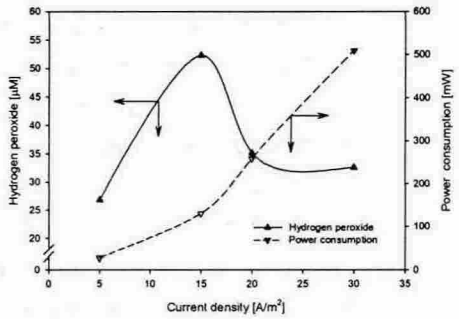

Fig. 2. H_2O_2 formation and power consumption at various current in an electrochemical membrane reactor. Temp=25℃, pH=7, O_2 sparging rate=50cm^{3}min^{-1}. Only electrolyte.

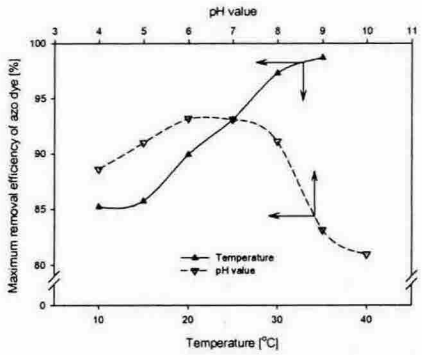

Fig. 3. Temperature (pH=7) and pH (temp=25℃) profiles.

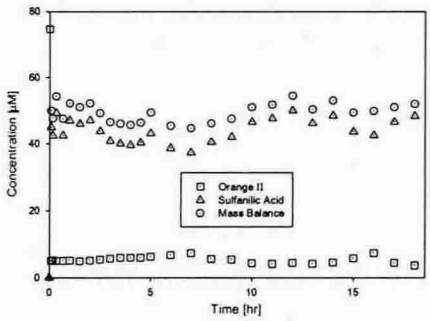

Fig. 4. Time-dependent mass balance of orange II and sulfanilic acid under the optimized operation.