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Enhanced Palladium Adsorption by Immobilized *Pichia pastoris*: A Reusable Catalyst for Reduction of 4-Nitrophenol

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Abstract

In this paper, the immobilized pellets were prepared by embedding *Pichia pastoris* (*P. pastoris*) with sodium alginate and used for the recovery of palladium ions in solution. The catalytic activity of immobilized Pd/*P. pastoris* for 4-nitrophenol (4-NP) was studied. The results showed that the recovery rate of Pd ions could be significantly increased by immobilized cells. The immobilized Pd/*P. pastoris* pellets showed good catalytic activity for the reduction of 4-NP, and the catalyst remained good catalytic activity even after multiple reuses.

Keywords

Palladium, Recovery, Immobilized, *Pichia pastoris*

1. Introduction

Due to its unique catalytic activity and high stability in selective hydrogenation and selective oxidation reactions, palladium is widely used as a catalyst in automobile exhaust purification, petrochemical industry and petroleum refining [1]. The reserves of palladium on the earth are very limited. The contradiction between the increase of palladium demand and the shortage of palladium resources will become more and more acute with the rapid development of industrial technology. Therefore, it is particularly important to develop effective technologies to make full use of existing resources and to recover palladium from waste.

It is well known that microbial cells can be used as adsorbents for metal ions due to their advantages of extensive sources, non-toxicity, mild reaction conditions and low cost. Different types of microorganisms have been proved to be

applicable to the recovery of palladium from the solution [2] [3] [4] [5]. However, the amount of metal ions adsorbed by microorganisms is still relatively limited. For some relatively high concentration metal solutions, a large amount of biomass is needed, which increases the difficulty of subsequent treatment. In recent decades, immobilization biological technology has been applied to biological fermentation, environmental purification, energy production and so on [5] [6] [7]. Microorganisms cells was embed in the carrier skeleton to protect them from the toxicity of pollutants, which not only increases the effective biomass, reduces the cost of cell reconstruction, but also shows good dispersion and recyclability [8] [9]. In this paper, *P. pastoris* were embed with sodium alginate to recover palladium from the solution, and the immobilized pellets with palladium were used as a supported catalyst for the reduction of 4-np.

2. Material and Methods

2.1. Materials

P. pastoris was purchased from Invitrogen. Palladium chloride, peptone, yeast extract powder, glucose, 4-nitrophenol, sodium borohydride ($NaBH_4$), and other agents used in the experiment were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals and reagents were used as received without further purification.

2.2 Biosorption of Pd(II)

P. pastoris were incubated in the medium containing 10 g/L yeast extract, 20 g/L peptone, and 20 g/L glucose at 30˚C for 48 h. The yeast was harvested by centrifugation at 3000 rpm for 10 min, rinsed twice with deionized water and freeze-dried. The biosorption experiments were performed by adding *P. pastoris* biomass into 100 mL of Pd(II) solutions, which was stirred on a shaker at a rotation rate of 150 rpm in the dark at 30˚C. Samples were taken at regular intervals for analysis.

0.7 g sodium alginate was dissolved in 50 mL of distilled water. Afterwards, it was mixed with the prepared *P. pastoris* yeast solution (10 mL) and released dropwise into 0.05 M $CaCl_2$ solution. The beads were soaked in $CaCl_2$ solution for 1 h to improve their mechanical strength and washed three times with distilled water to remove excess calcium ions. The biosorption experiments were conducted and samples were taken at regular intervals for analysis.

2.3 Characterization

Scanning electron microscopy (SEM; ZEISS Sigma) was applied to analyze the morphology of immobilized Pd/*P. pastoris.* Pd concentration was determined using atomic absorption spectroscopy (AAS, TAS990).

2.4 Catalytic Reduction of 4-NP

In a typical reduction experiment, 0.1 mL of 1 mmol/L 4-NP was mixed with 2.9

mL of 0.1 mol/L $NaBH_4$ solution in a quartz colorimetric dish and then three immobilized Pd/*P. pastoris* pellets were added. The UV-Vis absorption spectra at a given time were taken. The conversion ratio of 4-NP can be calculated by the followed equation:

$$\text{Conversion}(\%) = (1 - A_t / A_0) * 100. \quad (1)$$

After the reaction, the pellets were recycled from the solution by tweezers and rinsed with distilled water. The reuse catalytic activity was studied for several runs.

3. Results and Discussion

There were abundant functional groups in microbial cells surface such as sulfur, hydroxyl, carboxyl and other groups, which can be used as adsorbent to recover metal ion in solution through surface complexation, ion exchange, electrostatic attraction and other effects. Herein, *P. pastoris* was used as an adsorbent to study the effect of different initial palladium concentrations of on the adsorption efficiency. As shown in **Figure 1(A)**, the adsorption efficiency of palladium increases with the extension of reaction time. When the reaction time was 60 min, a dynamic equilibrium was reached and the adsorption rate of palladium was only 64.5%. Extending reaction time little influence has little effect on the Pd uptake. However, the adsorption ratio of palladium decreased with the increase of initial palladium concentration. Therefore, it is necessary to take some measures to improve the recovery efficiency of palladium.

In order to enhance the recovery efficiency of palladium, the immobilized pellets were prepared by embedding *P. pastoris* with sodium alginate. It can improve the dispersion and stability of microbe cell and avoid the loss of microbe in the reaction process. Moreover, the recycle process is facile. **Figure 2(A)** and **Figure 2(B)** are photos of the as-prepared immobilized pellets. The microspheres with a diameter of 3 mm are uniform and have good elasticity. The SEM

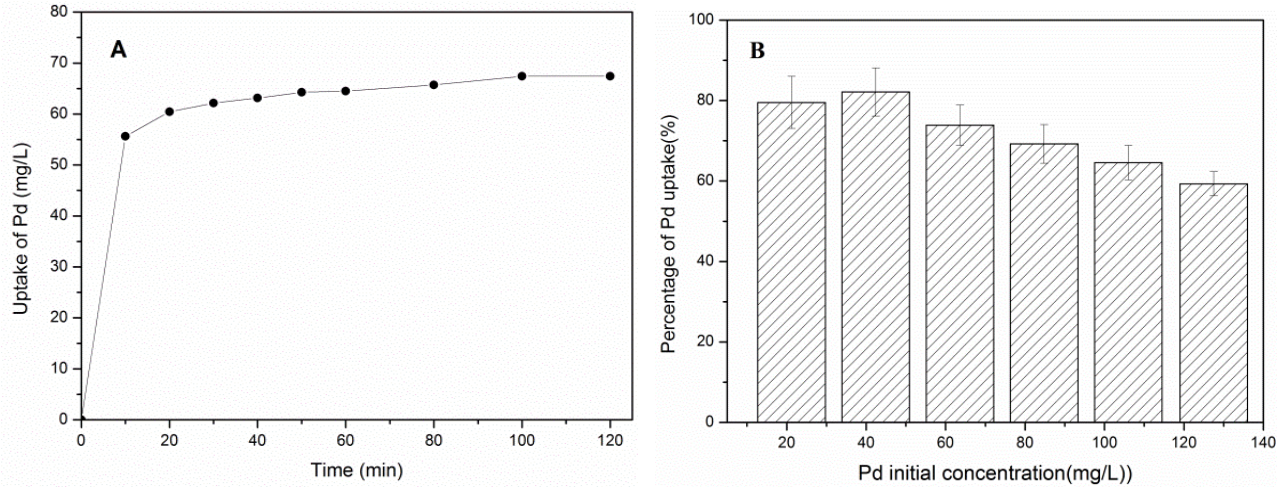

Figure 1. (A) Percentages of Au uptaken by *P. pastoris* versus time (*P. pastoris*: 4 g/L; Pd (II): 106 mg/L; 30˚C); (B) Effect of Pd initial concentration on the percentage of Pd uptake by *P. pastoris* (*P. pastoris*: 4 g/L; 30˚C; 120 min).

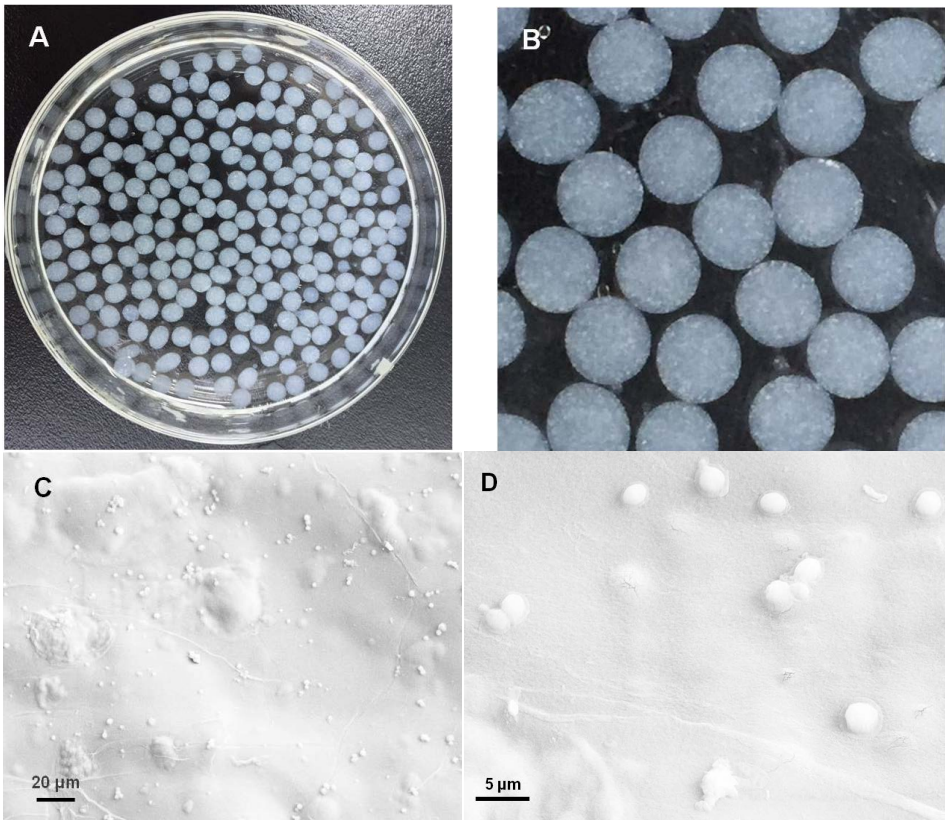

Figure 2. ((A), (B)) Photos and SEM images ((C), (D)) of immobilized *P. pastoris* cells.

images in **Figure 2(C)** and **Figure 2(D)** shows that *P. pastoris* evenly dispersed in the calcium alginate gel beads formed by the cross-linking reaction between sodium alginate and calcium divalent ions.

The immobilized pellets were used to adsorb palladium in the solution and the effects of different *P. pastoris* loads on the palladium adsorption were studied. As shown in **Figure 3**, even when *P. pastoris* loading capacity was 1 g, almost all palladium ions in the solution were absorbed at 2 h, indicating that the immobilization technique can significantly improve the recovery of palladium in solution.

4-NP is a kind of common organic pollutant in petroleum, medicine, chemical industry and other industrial wastewater. It is highly toxic and difficult to be biodegraded. Direct discharge will cause great harm to both biology and environment. It has been reported that 4-NP can be converted to p-aminophenol (4-AP) by sodium borohydride in the presence of catalyst [10] [11]. Herein, the immobilized pellets adsorbed with palladium (IPP) were served as heterogeneous catalyst for the reduction of 4-NP. As shown in **Figure 4**, the absorption peak at 400 nm gradually weakened with the extension of reaction time, indicating that 4-np was constantly converted to 4-AP. The conversion rate was nearly 85% at 10 minutes.

Although the conversion rate and conversion rate were decreased compared with the Pd/*P. pastoris* catalyst we reported previously [10], the IPP catalyst

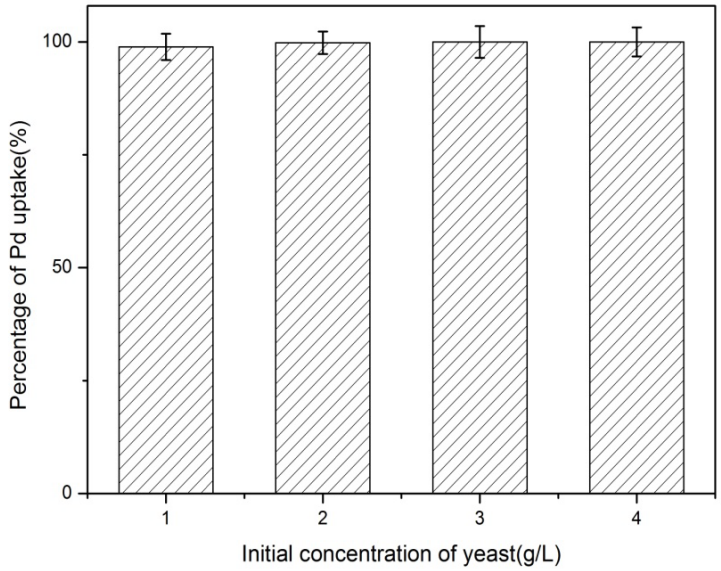

Figure 3. Effect of biomass concentration on the percentage of Pd uptake by immobilized *P. pastoris* (Pd(II): 106 mg/L, 30˚C, 120 min)

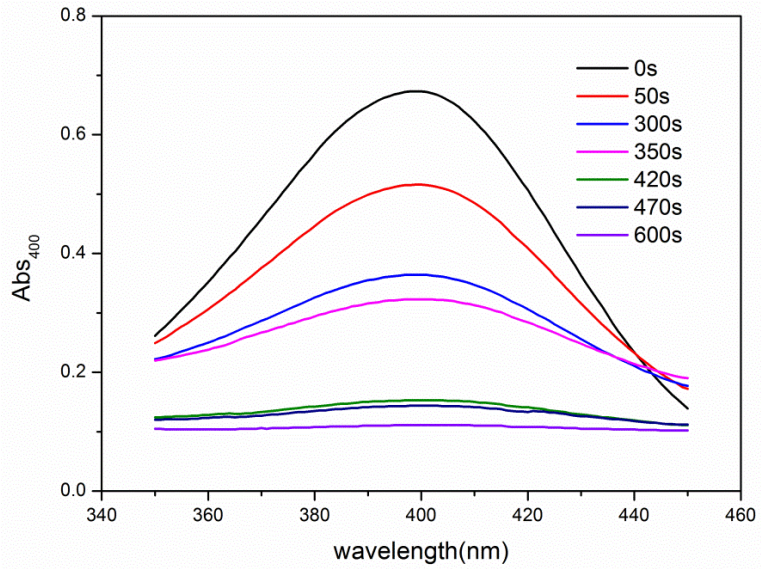

Figure 4. Time-dependent UV-visible absorption spectra for the reduction of 4-NP with immobilized Pd/*P. pastoris*.

used less at one time and the catalyst could be easily recycled, thereby reducing loss of catalyst during the reaction process. **Figure 5** shows the activity of different batches of recovered catalysts. The catalyst activity after the second recovery has been improved compared with the first recovery. That's probably because sodium borohydride further reduced Pd(II) adsorbed in the pellets to Pd(0) during the reaction process, increasing the proportion of Pd(0) in the pellets. Due to the double protection of the functional group on the surface of bacteria and calcium alginate gel, the active component Pd is not easy to agglomerate, leading to the good catalytic activity after repeated recovery.

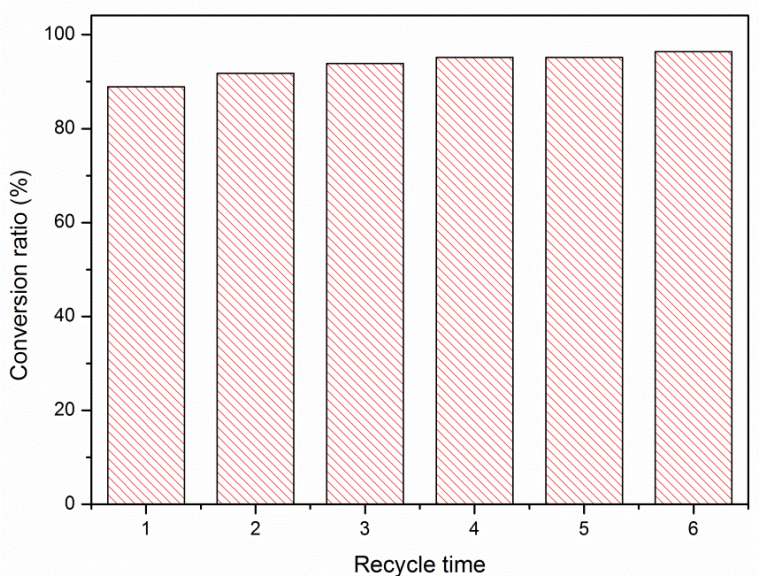

Figure 5. Recycling activities of Pd/IPPC for the catalytic reduction of 4-NP.

4. Summary

Compared with *P. pastoris* cells, IPPC pellets can significantly improved the recovery of Pd ions in solution. The immobilized pellets after Pd adsorption were not only easy to recover, but also exhibited good catalytic activity towards the reduction of 4-NP. This may be attributed to the double protection of the abundant functional groups on the cell surface and the calcium alginate gel framework, keeping the good dispersion of PCC and preventing the aggregation of the active components.

Acknowledgements

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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