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A Study of Pt^{4+} -Adsorption and Its Reduction by *Bacillus Megaterium* D01*

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The properties of Pt^{4+} -adsorption and its reduction by *Bacillus megaterium* D01 were studied by means of ICP, anode-stripping voltammetry, TEM, IR and XPS. The results of ICP analyses showed that the Pt^{4+} -adsorptive efficiency of the strain D01 was as high as 94.3% under the conditions of 100 mg Pt^{4+}/L, 1 g biomass/L, pH 3.5 and at 30 ℃ for 24 h. Moreover, it was confirmed from anode stripping voltammetry that the strain D01 possessed a strong reducibility. The TEM analysis indicated that the strain D01 was able to adsorb and reduce Pt^{4+} to Pt^0, small particles. The XPS result further supported the reduction of Pt^{4+} to Pt^{2+}, followed by the further recuction to Pt^0. The IR spectrum implied that D01 biomass adsorption of Pt^{4+} may result in the complexation of the C═O bond to the Pt species.

Keywords Biosorption, Bioreduction, Platinum, *Bacillus megaterium*
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Introduction

The accumulation of metals by microorganisms has been known for a few decades and has received more attention in recent years because of its potential application in environmental protection and the recovery of precious metals. There have been a number of reports on the biosorption of cadmium[1], chromium[2], uranium[3], lead[4,5] and gold[6,7] by microbial biomass. However, there have been only a few reports on platinum biosorption[8]. Brierey and Vance[8] reported that a metal removal agent(MRA) could efficiently remove acidic platinum($PtCl_4$) but the accumulation capacity was only 53 mg Pt/g MRA. Recently, we have reported the results of strain D01 screened from different source bacterial strains and identified as *Bacillus megaterium* D01, which exhibited a relatively strong ability of adsorbing Au^{3+}[9]. The strain D01 has been used as bioreductant for the preparations of highly dispersive supported gold catalyst[9,10] and bacteria-modified carbon paste electrodes used to determine the trace amounts of gold(Ⅲ)[11]. As a long program research on the bioreduction and the recovery of precious metals, here we will further report the results of Pt^{4+} -biosorption and bioreduction by strain *Bacillus megaterium D*01, which shows the strongest ability of adsorbing Pt^{4+} among the strains screened. The system of Pt^{4+} - D01 biomass and its reductive state

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were characterized with ICP, anode-stripping voltammetry, TEM, IR and XPS.

Experimental

1 Reagents and Methods

H_2PtCl_6 and other chemical reagents were of analytical purity. Pt^{4+} concentration was determined on a Baird PS-4 ICP-AES atomic adsorption spectrophotometer. The TEM was measured with a JEM 100 CXII transmission electron microscope. The voltammetric curves and the IR spectra were measured on a 8511A potentiostat and a 740sx FTIR spectrometer, respectively. The XPS were measured on a ESCALRB MKI X-ray photoelectron spectrometer.

2 Bacterial Cultivation and Biomass Preparation

Strain *Bacillus megaterium* D01 was cultivated according to the literature[9]. The cultures were harvested by centrifuging(3 500 r/min, 15 min) and the cell pellets were subsequently washed three times with deionized water. The washed biomass was dried at 60 ℃ and then grounded with a mortar and pestle. The dried biomass was stored in capped bottles in a dryer.

3 Biosorption Tests of Pt^{4+} and Calculation of Pt^{4+} Biosorptive Efficiency and Capacity

The D01 dried biomass was mixed with a H_2PtCl_6 solution. The mixture containing 100 mg Pt^{4+}/L and 1 g dried biomass/L was incubated on a rotary shaker at 130 r/min, pH 3.5 and 30 ℃ for 24 h. The mixture was filtered through a 0.22 μm pore-size cellulose acetate filter membrane and the filtrate was assayed with an atomic adsorption spectrophotometer for the determination of the residual Pt^{4+} concentration. The efficiency and the capacity of biosorption of Pt^{4+} ions were calculated with the following equations:

$$\text{Biosorptive efficiency of } Pt^{4+}\ (\%) = [(c_i - c_f)/c_i] \times 100\%$$

$$\text{Biosorptive capacity of } Pt^{4+}\ (\text{mg } Pt^{4+}/\text{g dry biomass}) = (c_i - c_f)/c_b$$

where c_i and c_f are the initial and final concentration(mg/L) of Pt^{4+} in the mixture, respectively, c_b is the biomass concentration(g/L).

4 Preparation of Samples for TEM micrographs and XPS

After platinum biosorption had been completed, the samples were taken out with the copper grids. The sample supported on the copper grids was dried at room temperature and then recorded with a transmission electron microscope at an accelerating voltage of 100 kV.

The biosorption test was carried out under the concentrations of 100 mg Pt^{4+}/L, 5 g biomass/L, and at pH 3.5 and 30 ℃ for the time required. The D01 biomass adsorbing Pt^{4+} was centrifuged and dried under a reduced pressure at 80 ℃ for 4 h. The samples were detected with a photoelectron spectrometer.

Results and Discussion

1 Biosorption of Pt^{4+} by Strain D01

According to the equations in the experimental section, the efficiency and the capacity of biosorption of Pt^{4+} by strain D01 reached as high as 94.3% and 94.3 mg Pt^{4+}/g dry

biomass, respectively. The residual amount of Pt^{4+} in the solution was 5.7 mg/L when the initial concentration of Pt^{4+} was 100 mg/L. The other strains showed a less biosorptive capacity than strain D01. The high efficiency of biosorption shows that strain D01 is a suitable strain for adsorbing Pt^{4+} and may be of potential application to the recovery of platinum.

2 Determination of the Reducibility of Strain D01 with Anode Stripping Voltammetry

To survey the reducibility of strain D01, the voltammetric curves of the system were determined with a D01 biomass-modified carbon paste electrode in a HCl solution at pH 4.0. A peak at 0.25 V appeared in the voltammetric curve obtained with the bacteria-modified paste electrode. In contrast, there was no peak in the voltammetric curve obtained with the unmodified electrode. This indicates that D01 biomass was oxidized electrochemically. The reduction potential(0.25 V) of D01 biomass confirmed that D01 biomass was able to reduce Pt^{4+}.

3 TEM of Pt^{4+} - D01 Biomass System

Fig. 1 is the transmission electron micrograph of D01 biomass exposed to an aqueous solution of H_2PtCl_6 at pH 3.5 and 30 ℃ for 24 h. It is obvious that there were small particles on the cell wall, which corresponded to Pt^0 in microform state reduced from adsorbed Pt^{4+}. This illustrates that D01 biomass possesses relatively strong abilities of not only adsorbing Pt^{4+}, but also reducing Pt^{4+} ions to Pt^0. The result was identical with that reported in the literature[8]. The MRA became dark red as the platinum was loaded which suggested the reduction of the platinum ions to the metallic platinum by the MRA.

Fig. 1 Transmission electron micrograph (×20 000) of D01 biomass contacted with Pt^{4+} for 24 h.

4 XPS Characterization of Pt^{4+} - D01 Biomass System

Fig. 2 shows the XPS spectrum of D01 biomass contacted with Pt^{4+} for 12 h. The peaks of bonding energy of 75.1, 74.6 and 71.8 eV seen in Fig. 2 were assigned to Pt^{4+} ($4f_{7/2}$), Pt^{2+} ($4f_{7/2}$) and Pt^0 ($4f_{7/2}$), respectively. It was estimated that about 60% of Pt^{4+} was reduced to Pt^{2+} and about 20% of Pt^{4+} was reduced to Pt^0. The evidence of XPS further supports the reduction of Pt^{4+} adsorbed by D01 biomass from an aqueous solution of H_2PtCl_6, which involved a reduction of Pt^{4+} to Pt^{2+}, followed by the further reduction of it to Pt^0.

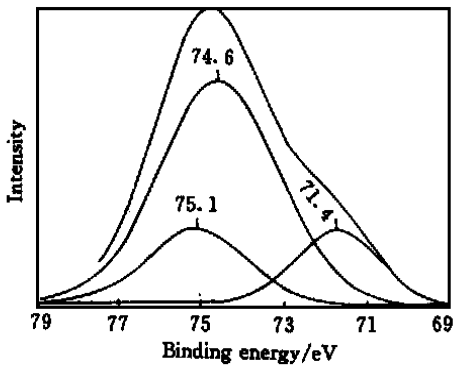

Fig. 2 XPS spectrum of Pt^{4+} reduced by D01 biomass for 12 h.

5 IR Spectra Characterization of Strain D01 Adsorbing Pt^{4+}

The IR spectra of the biomass and biomass contacted with Pt^{4+} solution for different time were compared. It was found that the peak at 1 664 cm^{-1} was decreased and shifted to 1 649

cm^{-1}, and the peak at 3 087 cm^{-1} also decreased and finally disappeared with increasing the interaction time of D01 biomass with Pt^{4+}. Usually, the IR spectral peaks at 1 664 cm^{-1} and 3 087 cm^{-1} belonged to $\nu_{as}(C=O)$ and $\nu_{as}(NH)$ of the peptide chain on cell wall, respectively[12]. The results mentioned above imply that D01 biomass adsorption of Pt^{4+} may result in the complexation of the C=O bond to the Pt species which makes the $\nu_{as}(C=O)$ shift to a lower frequency, indicating that the C=O bond is weakened to some extent. Moreover, the peak at 1 726 cm^{-1} corresponding to $\nu_{as}(COOH)$ disappeared after the interaction of it with the Pt^{4+} solution, indicating the complexation of free carboxylic acid.

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