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Recovery of Palladium(II) from nitric acid medium using a natural resin prepared from persimmon dropped fruits residues

Qingping Yi [a,b], Ruiyi Fan [a], Feng Xie [c], Qinglin Zhang [a,d], Zhengrong Luo [a,d,*]

[a] Key Laboratory of Horticultural Plant Biology, Huazhong Agricultural University, Wuhan 430070, China
[b] College of Bioengineering, Jingchu University of Technology, Jingmen 448000, China
[c] Institute of Horticultural Sciences, Jiangxi Academy of Agricultural Sciences, Nanchang 330200, China
[d] Hubei Collaborative Innovation Center for the Characteristic Resources Exploitation of Dabie Mountains, Huanggang 438000, China

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ABSTRACT

A natural resin, named “PPF resin”, was prepared by cross-linking persimmon tannin with formaldehyde and employed as adsorbents for selective recovery of Pd(II) from nitric acid medium. Parameters such as acidic media, HNO_3 concentration, contact time, initial metal concentration and temperature were investigated in detail. The adsorption behavior followed the typical monolayer type of Langmuir model and the maximum adsorption capacity reached 259.7 mg g^{-1} at 323 K. The obtained thermodynamic parameters (ΔG, ΔH and ΔS) revealed that this adsorption process was feasible, spontaneous and endothermic process. After adequately characterizing the samples by FT-IR, XRD, XPS and SEM-EDS, the adsorption mechanism was proposed to be complex formation and redox reaction. The Pd(II) recovery from industrial nitric acid extract of printed circuit boards was effective and highly selective, and the loaded Pd(II) can be easily desorbed using acidic thiourea solutions. Therefore, the present results provide a new, low cost and effective approach for palladium recovery from e-wastes in nitric acid medium.

1. Introduction

Palladium is one of the precious metals with increasing application in many fields such as electrical and electronic devices, catalysts, medicine, dentistry, jewelry, etc. The demand and price of palladium have been soaring in recent years [1]. In general, mineral ores for the extraction of palladium contain less than 10 g t^{-1} whereas the printed circuit boards (PCBs) of personal computers and mobile phones contain 110 g t^{-1} and 280 g t^{-1} of palladium, respectively [2]. It was reported that palladium made up around 50% of the economic value of the bare waste computer PCBs after the components were disassembled [3]. Due to lower ore reserve and the ever-increasing industrial applications, it is urgent and attractive to recover palladium from secondary resources in the viewpoint of environmental protection and resource saving.

To achieve the effective recovery of precious metals, several traditional methods including electrochemical technology, chemical precipitation, ion exchange, solvent extraction and membrane separation were employed [4]. But, adsorption is one of the widely used techniques for metal ions recovery from aqueous solutions [5,6], due to its operational simplicity, universal nature, high efficiency and availability of biomass and waste bio-products [7,8]. A variety of biomaterials have been developed for the recovery of precious metals including bacteria (*Escherichia coli*) [9], moss (*Racomitrium lanuginosum*) [10], lignophenol [11], collagen fiber [12], chitosan [13,14], cellulose [15], etc. Due to the inherent chemical structure of adjacent polyhydroxyphenyl groups, tannin-based adsorbents also have received huge interests and exhibited good sorption ability for metal ions such as Au(III), Pd(II), Pt(IV), Ag(I), Cr(VI), Pb(II), etc [16-20]. But for palladium adsorption, published studies have mainly focused on the recovery of Pd(II) from hydrochloric acid solutions, great efforts had been made to enhance the complexing ability by immobilizing N, S donor atoms ligands onto the persimmon tannin adsorbent, such as dimethylamine, bisthiourea, N-aminoguanidine and thiocyanate [17,21-23].

Currently, hydrometallurgical treatment for dissolving precious metals in PCBs is gaining popularity, the lixiviants are strong mineral acids like aqua regia, HNO_3, H_2O_2 in chloride media [22]. Unlike gold and platinum, palladium can be easily dissolved in high concentration of HNO_3 solutions, Pd(II)-bearing leach liquors frequently appeared in the actual industrial samples containing nitrate-rich acid solutions. Palladium is also found as a fission product from high level liquid waste in spent nuclear fuel, and the recovery of palladium from nitrate medium by solvent extraction and ion exchange has been widely investigated [24-26]. However, there is no literature involving the strategy of palladium recovery

* Corresponding author. Tel./fax.: +86 27 87282677.
E-mail address: luozhr@mail.hzau.edu.cn (Z. Luo).

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from PCBs in nitric acid solutions by biosorption. Therefore, investigations on the recovery of Palladium(II) from nitric acid medium are of actual significance for Pd(II)-bearing leach liquor.

Persimmon (*Diospyros kak*i Thunb.) has a wide distribution in China, Korea, Japan, Spain, Brazil, etc. Since they are abundantly available, low-cost and ecofriendly reusable, persimmon residues such as physiological dropped fruits, artificial thinning fruits and fruit peels can be employed as raw materials to produce persimmon powder containing large quantities of tannin. In our previous work, a natural resin, persimmon powder formaldehyde resin (PPF resin), has shown admirable potential towards gold recovery from aqueous solutions and harsh industrial acidic conditions [27,28]. The success achieved in this method incited us to extend the application to palladium recovery from Pd(II)-bearing leach liquor of PCBs. Herein, we describe a strategy of palladium recovery from PCBs by biosorption in nitric acid medium, and the aim of this paper is to initially investigate the adsorption behavior and mechanism of palladium onto PPF resin, and then to develop a low cost, eco-friendly method to recover Pd(II) from nitrate leached liquor of e-wastes.

2. Materials and methods

2.1. Materials

Astringent persimmon dropped fruits were used as raw material to extract tannin-riched persimmon powder, which was kindly donated by Huikun Agriculture Product Co. Ltd., Gongcheng, China. The PPF resin, a one-step assembly product, was simply prepared by immobilizing persimmon powder with formaldehyde according to the method reported previously [18]. Palladium(II) nitrate dehydrate (99.9%) was purchased from Yurui chemical. Co. Ltd., Shanghai, China. The working solution of Pd(II) was prepared by dilution from 1600 mg L^{-1} Pd(II) stock solution. All the other reagents applied in the present study were of analytical grade without any purification and purchased from Sinopharm Chemical Reagent Co. Ltd., Beijing, China.

2.2. Instrumentation

Metal ion concentrations of samples were measured by inductively coupled plasma optical spectrometer (ICP-OES, optima 2100) or atomic adsorption spectrophotometer (AAS, Virian Spectra AA 220).

Fourier transform infrared spectra (FT-IR) were recorded by Nicolet 6700 spectrophotometer using the KBr pellet method. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 advance diffractometer. X-ray photoelectron spectroscopy (XPS) was performed on a VG Multilab 2000 instrument. Scanning electron microscope (SEM) images and energy dispersive X-ray spectrometer (EDS) profiles were acquired using a Jeol JSM-5610LV instrument.

2.3. Batch adsorption studies

The influences of mixed acidic medium, HNO_3 concentration, contact time, initial metal concentration and temperature were studied in detail. A typical batch experiment was described as follows. Twenty milligram PPF resin and 20 mL Pd(II) working solution were mixed in the sealed conical flasks and shaken for 24 h at a speed of 200 rpm in a gas bath thermostat oscillator (SHZ-82). Then the mixture was filtered and the concentration of the filtrate was measured. The adsorption percentage (% *Adsorption*) and the amount of Pd(II) adsorbed on the adsorbent, q_t (mg g^{-1}), were calculated according to Eqs. (1) and (2), respectively.

$$\%Adsorption = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

$$q_t = \frac{C_i - C_e}{W} \times V \quad (2)$$

where C_i (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium concentration of metal ions in solution, respectively. W (mg) is the weight of adsorbent and V (mL) is the volume of the test solution. All the batch adsorption experiments were replicated three times and the errors were found to be within 5%.

The kinetic experiment was conducted with 40 mg L^{-1} of the initial Pd(II) concentration in 0.1 mol L^{-1} HNO_3, the samples were collected at different time intervals (5–2880 min) to determine the adsorption equilibrium time. For the isotherm study, varied initial concentrations of Pd(II) ranging from 40 to 360 mg L^{-1} were employed at 293, 303, 313 and 323 K, respectively.

2.4. Column adsorption-elution studies

A continuous-mode column experiment for Pd(II)-bearing industrial samples was carried out using a glass column (1 cm internal diameter and 30 cm height) equipped with a constant flow pump (DHL-A) and an automatic fraction collector (BSA-100). 800 mg PPF resin, immersed in deionized water for 12 h before use, was packed into the column. Then, the column was successively conditioned with deionized water for 12 h. The feed solution of Pd(II)-bearing liquor was percolated through the glass column at a constant flow rate of 0.1 mL min^{-1}, the effluent solutions were collected at 40 min intervals for measuring the metal ion concentration. After the column adsorption was saturated completely, the packed resin was conditioned by deionized water for 12 h. Subsequently, the elution of the loaded metal ions was carried out by using 0.5 mol L^{-1} thiourea prepared in 0.5 mol L^{-1} HCl. The eluted samples were also collected and the metal concentration in the eluted solution was measured.

3. Results and discussion

3.1. Effects of acidic medium and HNO_3 concentration

The chemical morphology of palladium in acidic medium is a key factor influencing the metal binding to the adsorbent. The predominant species of palladium is $[PdCl_4]^{2-}$ in HCl media [17,29], and the major palladium species is Pd^{2+} in HNO_3 media [30]. In this study, the acid medium were mixed by different volumes of 0.1 mol L^{-1} HCl and HNO_3 solution when the total volume and the concentration of H^+ ion were fixed at 20 mL and 0.1 mol L^{-1}, respectively. Fig. 1(a) shows the palladium adsorption capacity was negligible in 0.1 mol L^{-1} HCl (volume ratio = 20:0). The acidic medium containing fewer Cl^- and more NO_3^- were found to be favorable for the palladium adsorption onto the PPF resin. It is worth noting that PPF resin exhibited high affinity towards palladium in 0.1 mol L^{-1} HNO_3 (volume ratio = 0:20). This phenomenon can be explained by the distribution of palladium species in different acidic media, that is to say, the PPF resin has higher affinity for cationic Pd^{2+} than anionic $[PdCl_4]^{2-}$. Taking into account the fact that some Pd(II) bearing industrial samples appear in the nitric acid medium, the results are very promising for the recovery of palladium. Therefore, the nitric acid medium was chosen to conduct the following tests.

Fig. 1(b) shows the adsorption behavior of PPF resin towards Pd(II) at varying HNO_3 concentration (0.1-6 mol L^{-1}). Among the whole concentration, most of the palladium can be adsorbed onto PPF resin. However, the recovery rate declined rapidly with the