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Amino-bearing calixcrown receptor grafted to micro-sized silica particles for highly selective enrichment of palladium in HNO_3 media

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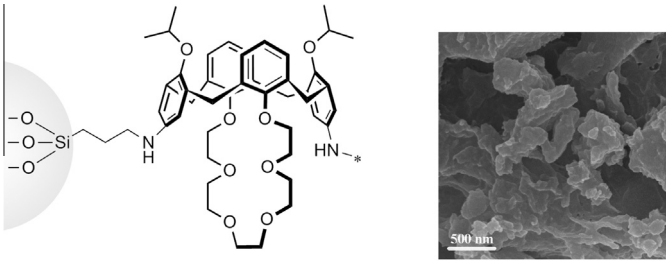
HIGHLIGHTS

- New silica adsorbent grafted with amino-bearing macrocyclic receptor.
- High selectivity and efficient adsorption of Pd(II).
- Kinetic fitting and isotherm modeling of the adsorption behavior.
- Chromatographic process for Pd(II) separation in high level liquid waste.

GRAPHICAL ABSTRACT

A new macrocyclic extractant was synthesized and grafted to micro-sized silica particles for selective enrichment of Pd(II) in high level liquid waste (HLLW).



Calixcrown receptor grafted to silica

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ABSTRACT

Palladium recovery in HNO_3-containing radioactive waste is of great value due to its considerable amount and benign radioactivity level. In this study, a new calixcrown receptor decorated with amino ligands (soft N donors) was synthesized for the selective extraction of Pd(II) in HNO_3 media. A high distribution ratio (D) of 278.6 was obtained within 10 min in solvent extraction. Moreover, the calixcrown receptor was covalently grafted to micro-sized silica particles to obtain a novel solid phase extraction (SPE) material (labeled as ACGSi). Detailed batch and column experiments revealed that the ACGSi material had fast kinetics and favorable adsorption capacity towards Pd(II) in HNO_3 solutions. Parameters influencing the adsorption ability such as contact time, acidity and initial metal concentration were fully evaluated. Kinetic equations (pseudo-first/second-order) and adsorption isotherm models (Langmuir and Freundlich models) were employed to fit the experimental data for inspecting the adsorption mechanism. On this basis, a facile chromatographic process was proposed for the selective enrichment and recovery of palladium in simulated high level liquid waste (HLLW). A recovery rate of 99.3% was obtained. The amino-decorated calixcrown extractant as well as the functionalized SPE material is believed to be promising to find applications in palladium separation from radioactive liquid wastes.

1. Introduction

Nowadays, palladium is being extensively consumed in various fields like catalysis and automotive catalytic converters [1,2]. Owing to the low natural abundance of palladium as well as the complexity in the refining process, however, people have been confronted with pressure about the imbalance between supply and demand of this precious metal. So it is of great importance to develop separation materials and methods for the recovery of palladium to meet the increasing demands. Industrial wastes such as spent catalyst and electronic components have been long recognized as a valuable source for palladium recovery. In recent years, it is urged that

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particular attentions should be paid to the fission palladium in the radioactive high level liquid waste (HLLW), which is generated during the reprocessing of nuclear spent fuels by Purex process [3,4]. As we know, the accumulated HLLW is constantly increasing worldwide because of the boom of nuclear power. According to a previous report, about 11 kg palladium could be generated in every metric ton of the spent fuels of fast reactor [5]. The full recovery would contribute a lot to the palladium metal obtained from natural sources. Moreover, among the six isotopes of fission Pd, the only radioactive isotope ^{107}Pd (17 wt.%), having a half-life of 6.5×10^6 years, is a soft β emitter (maximum energy 0.035 MeV), and the radiation intensity at the surface is only 520 Bq/cm^2 [6]. The nearly benign radioactivity level renders the fission Pd to be more favorably used in varieties of areas.

The well-known hydrometallurgical methods for palladium recovery are based on solvent extraction and solid-phase extraction (SPE) from hydrochloric acid media [7–10]. Considering the fact that concentration of the precious metal in environmental samples is at a considerably low level, a preconcentration/separation step is usually required for determination or recovery purpose, which can be better accomplished with SPE methods [11–21]. An major factor which needs to be taken into account is the selectivity to Pd(II), which relies upon the design and tailoring of the extractants. It has been suggested by Pearson that ligands bearing soft donor atoms like N, S should have affinity towards soft ion Pd(II). Great efforts have been made to investigate the complexing ability of amide derivatives and sulfur-containing extractants. However, most of these extractants lack unique selectivity to Pd(II) [11,14–16], and suffer from the drawback of slow kinetics to reach distribution equilibrium [12].

More recently, macrocyclic receptors such as crown ether [22], polythioether [23] and calixarene derivatives [24] have been found to show selective extraction towards Pd(II) [25]. The special complexation properties as well as the methods for Pd(II) separation by the use of these macrocyclic extractants soon aroused widespread research interests. For instance, Miyano et al. reported the synthesis of 'thiacalix[4]aniline', a cyclic tetramer of *p-tert*-butylaniline bridged with four sulfides, for the specific extraction of Au(III) and Pd(II) from acidic solutions among 41 interference ions including soft metal ions such as Hg(II), Pb(II), and Cu(II). It could be conclude from the experimental evidences that Au(III) and Pd(II) were extracted by forming complexes with thiacalix[4]aniline [26]. Typical researches aiming for ion recognition, transport and preconcentration of palladium were also carried out in Fontàs's group. NH-containing azamacrocycle [27] and thiacalix[4]arene derivatives [28,29] were prepared and loaded in supported liquid membrane (SLM) and solid phase extraction (SPE) systems for selective Pd(II) separation.

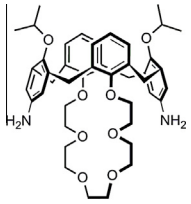
Nevertheless, it should be pointed out that the research on the complexing ability of macrocyclic compounds towards palladium is a new emerging area currently. The complexation models are still limited in number, and efforts should be further made to clarify the extraction mechanism. Besides, so far, the focus of most concern in this area has been always the extraction behavior towards palladium in chloride solutions, in which the solution chemistry of Pd has been extensively studied. However, with respect to the palladium separation in HNO_3 media, which will be of direct benefits to the recovery of this noble metal in radioactive liquid waste, much less attention has yet been paid to [3].

In this study, we present a new calixcrown receptor (1,3-alternate calix[4]arene-crown-6 derivative) for the highly selective extraction of palladium in HNO_3 solutions. The calixcrown compound was deliberately decorated with two amino ligands at the rotated benzene rings to promote complexing ability to the soft Pd(II) ion. The extraction ability towards Pd(II) was initially testified in solvent extraction system. Then, the calixcrown receptor was covalently bonded to micro-sized silica substrate through a post-grafting method to obtain a SPE material, which was labeled as ACGSi (Abbreviation for Amino-bearing Calixcrown Grafted Silica) in this study. Detailed investigations concerning the adsorption behavior to Pd(II) in HNO_3 media were performed by batch and column operations. Influencing factors including acidity, contact time and metal concentration were evaluated. On this basis, a chromatographic process was proposed for the selective enrichment of palladium from simulated high level liquid waste (HLLW).

2. Experimental

2.1. Chemicals

1,3-Di(2-propoxy)calix[4]arene-crown-6 was synthesized following the method reported by Ungaro's group [30]. Soft donor N atoms in the form of amino groups were then site-selectively introduced to the calixcrown molecule through a two-step reaction. The structure of the amino-decorated calixcrown receptor (1) was confirmed by ^{1}H/^{13}C NMR and FT-IR spectra [31].



(1)

Simulated high level liquid waste (HLLW) was prepared with metal nitrates in 1.0 mol/L HNO_3. The concentration of each metal ion was shown in Table S1, which is based on the estimated values of HLLW obtained during the reprocessing of spent fuels from a typical light water reactor (LWR) nuclear power plant. Tetramethoxysilane (TMOS), 3-chloropropyltrimethoxysilane (CPTMS) and di-*n*-butyltin dilaurate (DBTL) were supplied by Aldrich. Deionized water (resistivity > 18 MΩ cm) was produced by a Milli-Q water purification system. Analytical chemicals such as nitric acid, dichloromethane, metal nitrates, and other reagents were commercially purchased and used as received without further purification.

2.2. Characterization

^{1}H/^{13}C NMR and ^{13}C/^{29}Si solid-state NMR spectra were recorded by JOEL JNM-ECA600 NMR Spectrometer and Bruker AV300 Spectrometer, respectively. FT-IR spectra were obtained by Nicolet Nexus 470 FT-IR Spectrometer. Elemental analysis of C, H and N was performed on Elementar Vario EL III. N_2 adsorption–desorption isotherms were measured by NOVA 3200e Surface Area & Pore Size Analyzer. Samples were dried at 140 °C vacuum environment for at least 3 h before the nitrogen adsorption experiments. Specific surface areas were calculated based upon the Brunauer–Emmett–Teller (BET) method. The size and distribution of the samples was measured by MALVERN 2000 laser particle analyzer. The micro-morphology of the adsorbent particles was recorded by FEI Quanta 200 environmental scanning electron microscopy (ESEM). Metal concentration was measured by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (SPECTRO ARCOS SOP).

2.3. Preparation of the ACGSi material

The calixcrown receptor decorated with two amino ligands was chemically bonded to silica substrate by post-grafting method. Detailed synthesis can be seen our previous report [31]. Here, we briefly describe it as follows. Firstly, a silica-based precursor