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Organic–inorganic based nano-conjugate adsorbent for selective palladium(II) detection, separation and recovery

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HIGHLIGHTS

- Nano-conjugate adsorbent (NCA) is able to capture Pd(II) from acidic solution.
- The color formation indicates the Pd(II) detection without using high-tech instruments.
- The NCA has exhibited a high sorption capacity due to spherical nanosized cavities.
- The NCA is reversible and reusable without any significant deterioration.

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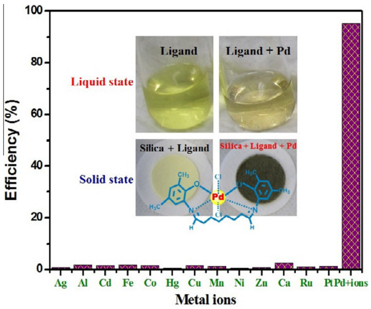
GRAPHICAL ABSTRACT



ABSTRACT

The functional group containing organic ligand of *N*,*N*(octane-1,8-diylidene)di(2-hydroxy-3,5-dimethylaniline) (DHDM) was developed and then successfully anchored onto mesoporous silica for the preparation of nano-conjugate adsorbent (NCA). After fabrication, the DHDM kept open functionality for capturing palladium (Pd(II)) under optimum conditions. The NCA exhibited the distinct color formation (π–π transition) after adding the Pd(II) ions both in solid and liquid states. The solution pH played an important role in the detection and sorption of Pd(II) but the prepared NCA worked well in the acidic pH region at 1.50. The data also clarified that the NCA did not form any color and signal intensity even in the presence of diverse ions except Pd(II). The determined limit of detection to Pd(II) ions was low as 0.14 μg/L. In Pd(II) sorption, the affecting factors such as solution pH, kinetics, isotherm models, competing ions and elution/regeneration were studied in detail. The NCA confirmed the rapid sorption property and the maximum sorption capacity was 213.67 mg/g due to spherical nanosized cavities with large surface area and pore volume. The base metal of Cu(II) and Zn(II) did not hamper the Pd(II) sorption ability of NCA in the acidic pH region. Therefore, it was expected that the Pd(II) could be separated from other hard metal ions by the NCA. The data also clarified that the other competing metal ions did not decrease the Pd(II) sorption capacity and NCA had almost no sorption capacity, which suggested the high selectivity of Pd(II) ions by NCA. The adsorbed Pd(II) was eluted with 0.20 M HCl–0.20 M thiourea eluent and simultaneously regenerated into the original form. The NCA was reversible and kept remaining functionality for reuse in many cycles after an extraction/elution process without significant deterioration. Therefore the proposed NCA can be considered as a potential candidate for Pd(II) capturing from waste samples.

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1. Introduction

The precious metal consumption is increasing in recent years due to the development of catalytic systems in automotive exhaust and the petrochemical industry. Of these precious metals, palladium (Pd(II)) is of great value in various fields with a wide variety of applications such as jewellery, fuel cells, automotive catalytic converters, pharmaceuticals, telecommunication, petroleum industry, electronics, heat and corrosion resistance apparatus and dental medical devices [1–3]. Similarly, Pd(II) can bind to thiol-containing amino acids, proteins, DNA, and several biomolecules and adversely affect the cellular processes [4]. In addition, fission Pd(II) is generated during the reprocessing of spent nuclear fuels and high level radioactive liquid waste is increasing due to boom of nuclear power worldwide [5,6]. Furthermore, the release of Pd(II) and its accumulation in the environment can cause the human health problems such as eye irritation, skin problems, rhinoconjunctivitis, asthma, etc. [7,8]. Therefore, the Pd(II) is strictly limited to be 5–10 ppm level by the European Agency for the Evaluation of Medicinal Products [9]. Thus, the research on the effective monitoring, separation and recovery of Pd(II) is of great importance and in high demand.

Many analytical methods have been developed to determine the presence of Pd(II) ions in clinical, environmental, industrial, and pharmaceutical samples such as spectrophotometry, atomic absorption spectrometry, solid phase microextraction-high performance liquid chromatography, X-ray fluorescence, electrochemical methods, inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) [10–14]. However, many of these are limited by instrumentation cost, high training requirements, being cumbersome, time consuming and unsuitable, especially in developing or less developed countries [15,16]. From the stand point of analytical chemistry, there is increasing demand to develop reliable, selective, sensitive and robust methods to quantify and detect the Pd(II) ions in complex samples matrices. The reaction-based monitoring approaches have demonstrated great advantages in-terms of selectivity and sensitivity for scientists [13,17,18]. They allow direct analysis of the specific elements by visual color optimization. However, many of these sensing systems have been suffering from rigorous test conditions and long response time. Therefore, the design of some novel and effective colorimetric methods for Pd(II) detection that have a rapid response, are cost-effective, easy to use and capable of being used in the field without reference solution is still required.

The conventional method for Pd(II) separation is chemical precipitation. This process has several disadvantages such as slow kinetics and solid–liquid-separation, huge chemical consumption and high labor requirements. Also the process increases environmental pollution due to the use of toxic chemicals. Solvent extraction (liquid–liquid extraction) is generally used for the separation and recovery of Pd(II) ions based on the soft donor atoms like ‘S’ and ‘N’ containing ligands [19,20]. However, many of these ligands have some drawback such as pH sensitivity, chemical stability and slower kinetics of extraction. The high cost of these compounds has been a major hurdle in their use in the large-scale process for potential applications in Pd(II) separation and recovery. There are also several methods that have been reported to treat Pd(II) solutions such as electro-deposition, ion exchange, membrane separation and adsorption [21–23]. Adsorption techniques have been extensively applied in the fields of analytical chemistry and separation chemistry based on fast kinetics, with wide possibilities of functionalization, high enrichment factors, less time consumption and producing a low amount of secondary wastes [3,8,24]. Different materials, such as chelating resins, chemically-modified activated carbon, functionalized silica, nanotubes, biomass or bio-adsorbent [20,25–31] have been used as adsorbents. However, most of the separation methods still suffer from low selectivity and sensitivity that limit their practical application. In connection to this, we have used different ligand functionalized mesoporous silica based materials for various metal ions monitoring and recovery under optimum conditions [11,16,26,32]. The ligand functionalized materials have gained special attention due to their high surface area, long mechanical stability, high sorption efficiency, high selectivity and sensitivity.

In this study, we prepared functionalized ligand immobilized nano-conjugate adsorbent (NCA) based on organic–inorganic combination for efficient and sensitive Pd(II) detection and recovery from waste samples. For preparation of the NCA, a *N*,*N*(octane-1,8-diylidene)di(2-hydroxy-3,5-dimethylaniline) (DHDM) was incorporated into mesoporous silica by non-specific interaction via hydrogen bonding, Van der Waals forces and reversible covalent bonds according to direct immobilization approach. Based on Pearson Hard–Soft Acid–Base (HSAB) theory, the soft metal ions such as gold(III) and Pd(II) ions has high affinity to soft bases with donor atoms as N > O [33]. The DHDM contained N and O donor atoms and exhibited a stable complex formation tendency with Pd(II) at specific pH area. The detection data was also performed even in the presence of diverse competing ions. The sorption and sensing experiments were carried out by both methods. Several influencing parameters such as solution acidity, kinetics, initial metal concentration, foreign ions, sorption capacity, color optimization and elution condition were evaluated. The DHDM has excellent intramolecular charge transfer structure and desirable colorimetrical properties and suitable for potential application in environmental and waste samples. It is also noted that the developed materials based on direct organic–inorganic composition are cost-effective and suitable to the large-scale treatment for Pd(II) detection and recovery.

2. Materials and methods

2.1. Materials

All materials and chemicals were of analytical grade and used as purchased without further purification. Tetramethylorthosilicate (TMOS), the triblock copolymers of poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) designated as F108 ($EO_{141}PO_{44}EO_{141}$) and 1,8-Octanediol were obtained from Sigma–Aldrich Company Ltd. USA. For pH adjustments in optical detection, buffer solutions of 3-morpholinopropane sulfonic acid (MOPS), 2-(cyclohexylamino) ethane sulfonic acid (CHES) and *N*-cyclohexyl-3-aminopropane sulfonic acids (CAPS) were procured from Dojindo Chemicals, Japan, and KCl, HCl, NaOH from Wako Pure Chemicals, Osaka, Japan. The standard Pd(II) ions solutions, and other metal salts for the source of diverse metal ions were purchased from Wako Pure Chemicals, Osaka, Japan. Ultra-pure water prepared with a Millipore Elix Advant 3 was used throughout in this work.

2.2. Synthesis and characterization of DHDM ligand

The structure and preparation of the *N*,*N*′-(octane-1,8-diylidene)di(2-hydroxy-3,5-dimethylaniline) (DHDM) is shown in Scheme 1. The DHDM was prepared by the reaction of 1,8-Octanediol (one moles) and 2-hydroxy-3,5-dimethylaniline (two mole) in ethanol and a small amount of acetic acid was added. The resultant mixture was then heated under reflux for 4 h and left to cool at room temperature. The solid formed upon cooling was collected by suction filtration. The separated product was recrystallized