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学位論文題目　Development of Poly(N-phenylglycine)-Based Adsorbent for Precious Metals Recovery and Study on Adsorption Mechanism
(ポリ-N-フェニルグリシン吸着剤の開発及び吸着メカニズムと貴金属のリサイクルに関する研究)


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# 論 文 内 容 要 旨

Today's global society is economically and socially dependent on minerals and metals. Terrestrial mineral deposits are by definition ‘non-renewable’ over human timescales, and their stocks are thus finite. Due to the large-quantity mining and consumption of metal resources, the decreasing grade of metal resources in the earth's crust greatly increases the mining difficulty and cost. Precious metals, such as gold and silver, are rare with high economic value, and also widely used in many fields. The imbalance between metal supply and demand is a major concern worldwide. At the same time, the increasing waste generated by electrical and electronic equipment has drawn more and more attention. The sustainable utilization of metal resources urgently requires the metal recovery from the urban mine—e-waste.

The main methods of metal recovery start with a physical pretreatment, followed by pyrometallurgy, hydrometallurgy. For precious metals, hydrometallurgy has advantages of less release of hazardous substances, more suitability for the treatment of low-grade raw material. In the final step of hydrometallurgy, an appropriate method is essential for the recovery of precious metals from leaching solutions. Among them, adsorption method offers advantages, because they are simple in process without secondary pollutants. Conventional adsorbents, such as activated carbons, shows limited adsorption capacity and selectivity. In the past few years, nanomaterials, including inorganic nanomaterials, organic polymer-support nano composites, and metal-organic frameworks (MOFs) nanomaterials, have been applied in the capture and isolation of precious metals ions due to their unique physical and chemical properties, including large surface area, high reactivity, developed porosity, and diverse functional groups. Conductive polymer, Poly-N-phenylglycine (PNPG), is an emerging polymer adsorbent used in adsorption studies, but its adsorption study on precious metals has not been reported so far.

Therefore, the purpose of this study is to develop PNPG-based adsorbent materials, study the adsorption mechanism towards representative precious metals ions (gold and silver), and recover them from the leaching solutions of waste electronic substrate, etc. Firstly, it has been proved that the nanoscale PNPG particles have a good adsorption ability towards gold ions, but their nanoscale structure will bring about the separation problem after adsorption. To reduce the separation burden, we proposed a strategy making PNPG particles into PNPG membrane, so that it can be rapidly separated after adsorption. Subsequently, the adsorption mechanism towards gold and silver ions was elaborated with the aid of a series of characterization techniques. Besides, the adsorption studies related to composite membranes showed the improved adsorption performance as well as membrane stability, providing a theoretical basis for the actual metal recovery application in the future. Finally, the selectivity of gold and silver was investigated by adsorption experiments from both experimental mixed solutions and real leaching solution of printed circuit boards, and the results indicated the possibility of metals recovery by PNPG-based adsorbents.

The main contents of the paper are arranged as follows.

Chapter 1 showed the research background, research significance, and research topic studying the PNPG-based adsorbent for precious metals recovery and providing the basic theory for practical application.

Chapter 2 summarized and presented the detail information about materials and equipment, as well as the preparation method of PNPG particles, PNPG membranes, and composite membranes of PNPG and multi-walled carbon nanotube.

In chapter 3, PNPG particles were first used to capture gold with adsorption capacity (1356.78 $mg \cdot g^{-1}$) and good sensitivity to Au(III) in low-concentration solutions at pH 1. The mechanism of Au(III) adsorption by PNPG mainly involved chemisorption and monolayer adsorption, as evidenced by the well-fitting pseudo-second-order model (PSO) and Langmuir isotherm model. Electrostatic interactions and redox reactions occurred during adsorption, as characterized by zeta potential, XRD, TEM, FT-IR, and XPS. To solve the problem of removing the adsorbent after adsorption, the PNPG membrane was prepared in advance by vacuum filtration, and corresponding stability test experiments were conducted. SEM characterization revealed that the support layer did not participate in the adsorption process. The PNPG membrane remained active for a minimum of three cycles and could selectively capture Au(III) from uneven-concentration polymetallic solutions. Approximately 80% of the gold in the leaching solution of waste printed circuit boards of computers was selectively recovered using the prepared 2-mg PNPG membrane, proving the possibility of practical application of PNPG membranes for the recovery of gold from e-waste.

Chapter 4 is about the Ag(I) adsorption by PNPG membrane. In this chapter, the PNPG membrane was prepared by the same method as before. The characterization studies were also performed to elucidate the reaction mechanism between the PNPG membrane and Ag(I). It was found that most benzenoid diamine structures undergo a redox reaction with Ag(I), while a minority undergoes chelation which was different from the mechanism of Au(III) adsorption by PNPG. Through studies on the pH influence, adsorption kinetics, and adsorption isotherms, the maximum adsorption capacity was 366 $mg \cdot g^{-1}$ at pH 6, and this Ag(I) adsorption process also fitted well with PSO and Langmuir models. In particular, the PNPG membrane showed potential for the recovery of Ag from real solutions when leaching solutions of e-waste and municipal solid waste incineration fly ash were subjected to adsorption experiments.

Chapter 5 introduced the preparation and characterization of PNPG-based composite membrane, and the adsorption performance towards gold ions. PNPG decorated with multi-walled carbon nanotube (MWCNT) composite membranes (PNPG@MWCNT) was easily prepared using ultrasound-aided vacuum-assisted filtration and showed high stability. The results showed that MWCNT bound to PNPG through non-covalent interactions. The PNPG@MWCNT composite membrane with a mass composition of P3.5M0.5 showed an approximately 20% higher adsorption efficiency than the pure PNPG membrane after 24 h adsorption in acidic Au(III) solution with pH = 1. The Au(III) adsorption capacity was up to 1262.6 $mg \cdot g^{-1}$ at pH 1, and the well-fitted pseudo-second-order kinetic and Langmuir isothermal models indicated that the adsorption process was mainly chemisorption and monolayer adsorption. More importantly, the characterization data confirmed that the adsorption mechanism between composite membrane and Au(III) included electrostatic interactions and redox reactions, and the electron transfer from PNPG to MWCNT promoted the adsorption capacity. Furthermore, the results of all competitive adsorption, repeatability, and gold recovery experiments in the leaching solution of waste printed circuit boards also demonstrated the potential of the PNPG@MWCNT composite membrane in practical applications of gold recovery.

In chapter 6, the general conclusions outlook of this thesis was presented.

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# 論文審査結果要旨

本論文は、導電性高分子ポリマーであるポリ-N-フェニルグリシン（PNPG）を貴金属の吸着剤として提案し、吸着剤の開発及び吸着メカニズムと貴金属のリサイクルへの適用を検討したものである。本論文は全6章で構成されている。

第1章は緒論として、貴金属のリサイクルやPNPGに関する既存の研究から本研究の背景を述べ、研究目的を示している。第2章では、材料、装置および各種のPNPG吸着剤の作製方法について説明している。第3章では，作製したPNPG微粉末状吸着剤を用いて、Au(III)イオンの吸着および吸着メカニズムを検討している。結果として、従来の活性炭吸着剤の3倍以上の高い吸着容量（1357 mg Au/g）が得られた。PNPGによるAuに対する吸着メカニズムは主に化学吸着と単分子層吸着であることと、静電相互作用—酸化還元反応により吸着容量を向上させることを明らかにしている。また、吸着後の吸着剤微粉末と浸出液の固液分離問題を解決するために，真空ろ過法によりPNPG膜吸着剤を作製し、共存金属イオンを含む廃プリント基板の浸出液からAu(III)の選択的吸着を確認している。第4章では、PNPG膜吸着剤によるAg(I)イオン吸着および吸着メカニズムを調べている。結果として、従来の活性炭吸着剤の3倍以上の高い吸着容量（366 mg Ag/g）が得られた。Ag(I)の吸着メカニズムは、主にベンゼノイドジアミンとAg(I)の酸化還元反応であることを明らかにしている。また、E-wasteやごみ焼却飛灰の浸出液から、93%以上の回収率で選択的Agを回収することができた。第5章では、PNPGと多層カーボンナノチューブ（MWCNT）を用いて、PNPG複合膜（PNPG@MWCNT）吸着剤を作製し、金の吸着およびメカニズムを検討している。結果として、複合膜吸着剤は純PNPG膜より安定性が大幅に改善され、吸着容量も20%増加した。吸着能力の向上は、PNPGからMWCNTへの電子移動によるものを明らかにしている。また、競合吸着実験、吸着剤再生実験および実廃棄物浸出液から100%の金回収率などの結果から、PNPG@MWCNT複合膜による金のリサイクル技術の実用化の可能性を示唆している。第6章は結論であり、研究結果をまとめている。

本論文の成果は、その学術的な価値が高く、実用における課題を解決している観点から工学的な貢献も大きい。また、研究業績として、査読付国際学術誌論文3編、国内会議2件を公表している。

よって、本論文は博士（工学）の学位論文として合格と認める。