Dissertation Abstract

Recovery of Precious Metals from Waste Resources Using Dithiocarbamate-Functionalized Cellulose

Graduate School of Natural Science & Technology

Kanazawa University

Major Subject: Division of Material Chemistry

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School Registration No.: 1824022002

Name: FONI BUSHON BISWAS

Chief Supervisor: Prof. Hiroshi Hasegawa

Abstract

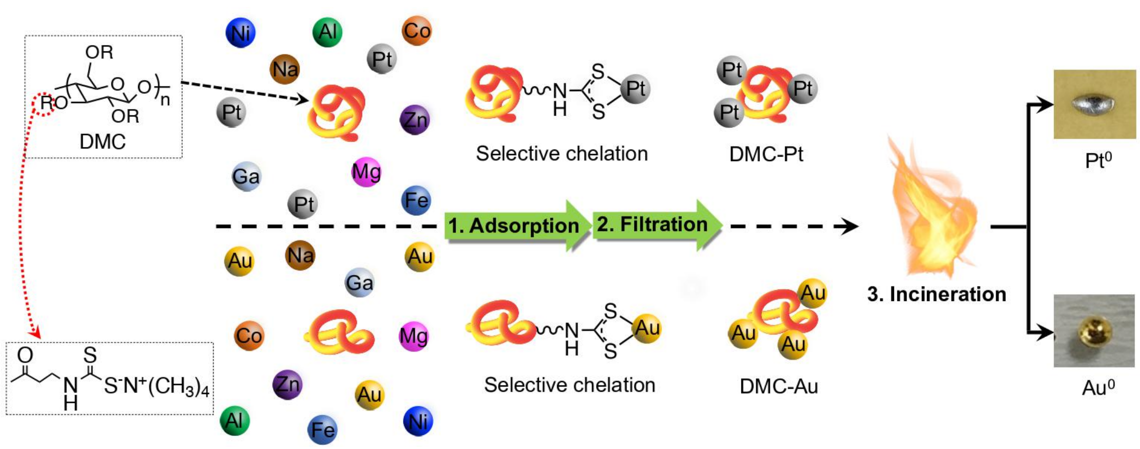
Recovery of precious metals (PMs) like silver (Ag), gold (Au), palladium (Pd), and platinum (Pt) from waste sources is of considerable importance due to several factors, such as their scarcity, economic importance, imbalance in supply-demand ratio, and toxicological effects. However, the reported work has focused only on the extraction process of PM ions from solution, while their subsequent recovery in pure and metallic form has been largely ignored. Moreover, most of the reported bio-sorbents have drawbacks of poor selectivity, low to medium sorption capacity, and slow sorption kinetics. The present study is focused on developing a simple and efficient approach for the selective extraction of PM ions from acidic solutions using bio-adsorbent, dithiocarbamate-modified cellulose (DMC), followed by subsequent recovery in elemental form. Batch adsorption experiments were carried out to investigate the adsorption properties of DMC against PM ions in terms of the effects of solution acidity, competing ions, agitation rate, contact time, temperature, and initial concentrations of PM ions. The following issues have been reported based on this study: (a) selective adsorption of PM ions from acidic solutions by DMC, and evaluation of the adsorption kinetics and isotherms models, (b) insight study of the adsorption mechanism of PM ions by DMC, (c) post-adsorption recovery of PMs in their pure and elemental forms via incineration of PMs-loaded DMC, (d) verification of the overall process for the recovery of PMs from real waste samples, and (e) a detailed comparative study of the sorption performance of DMC and some selected commercial resins for the recovery of PMs from industrial wastes.

EXTENDED DESCRIPTION

Precious metals (PMs) such as silver (Ag), gold (Au), palladium (Pd), and platinum (Pt) have widespread applications in versatile fields. The natural resources of PMs (high-grade ore) are diminishing while the demand is increasing. Although elemental PMs are nontoxic, their ionic forms (i.e., Ag^{I}, Au^{III}, Pd^{II}, and Pt^{IV}) are known to have toxic effects on living organisms and human health. Therefore, extraction and recovery of PMs from waste sources (e.g., industrial wastewater, sludge, e-waste, etc.) is crucial to mitigate imbalance in supply-demand ratio and waste-induced ecotoxicity. Nowadays, the commercial materials used for PM recovery include chelating or ion-exchange resins prepared using synthetic polymers, namely PS-DVB or PA-DVB as matrices. Although resins have high mechanical and chemical stability, they are non-biodegradable and considered toxic to the environment and animals. In addition, commercial resins are costly, display low to moderate sorption capacity, and are hindered in the sorption of PMs from waste solutions by the presence of coexisting ions. Considering the bioavailability, economic, and ecological concerns, synthetic polymer-based commercial resins for PM recovery should be replaced by efficient bio-sorbents. Extensive research has been carried out on the development of bio-sorbents for the extraction of PM ions. However, the practical application of these adsorbents has been limited owing to their reduced mechanical strength, low to moderate adsorption capacity, or slow adsorption kinetics. Another critical concern is the post-sorption recovery of PMs in their pure and elemental forms. In the conventional adsorption-desorption method of PM recovery, after extraction of the metal ions by an adsorbent, the desorption of metal ions is achieved using toxic eluents, such as acidic thiourea, sodium/potassium cyanide, and EDTA. Besides, the recovery process is highly laborious and complicated, costly, and inefficient. It is also worth mentioning that the subsequent recovery of PMs in their metallic form is ignored in most of the literature. Therefore, there is a need to develop a straightforward technique for the recovery of PMs in their corresponding elemental form.

Cellulose, the most abundant and renewable polymer, contains many hydroxyl groups, which could be utilized for functional modification. According to Pearson's hard-soft acid-base (HSAB) theory, Lewis soft base sulfur (S) atoms-containing functional groups, such as dithiocarbamate (DTC), shows a strong affinity for PM ions (Lewis soft acid), whereas a significantly weaker interaction to the intermediate/hard acid base-metal ions. Hence it was expected to have better selectivity and adsorption capacity of dithiocarbamate-modified cellulose (DMC) to capture soft acid PM ions using. Based on the abovementioned facts, the following research was conducted and reported emphasizing the selective extraction of PM ions from aqueous matrices using bio-sorbent, DMC, and subsequent recovery of PMs in their corresponding elemental forms.

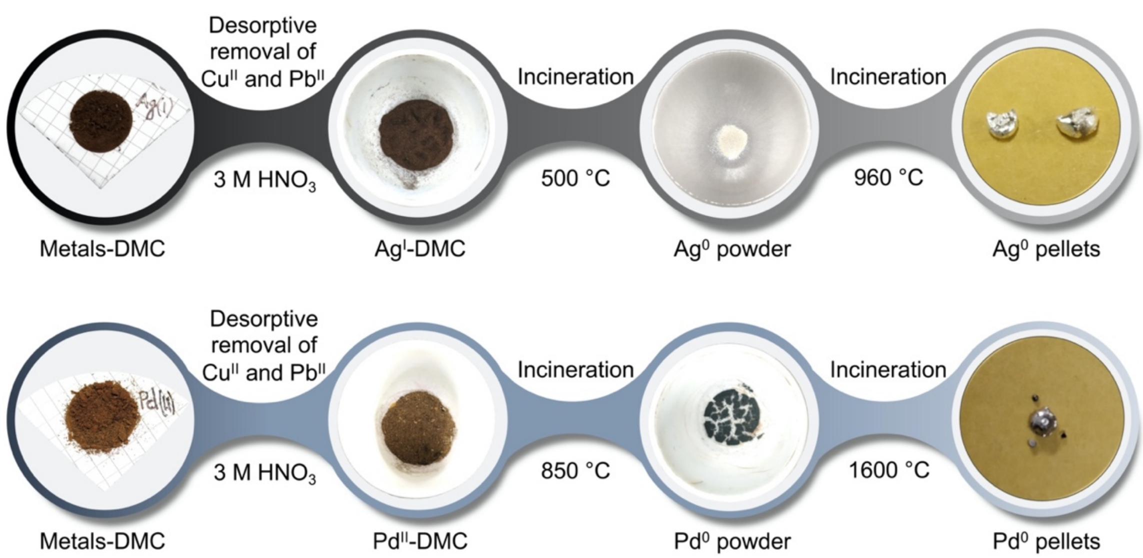
(a) Recovery of gold and platinum from aqueous matrices



A new approach has been explored for the recovery of Au and Pt using earlier developed bio-adsorbent, DMC. The adsorbent exhibits excellent adsorption efficiency

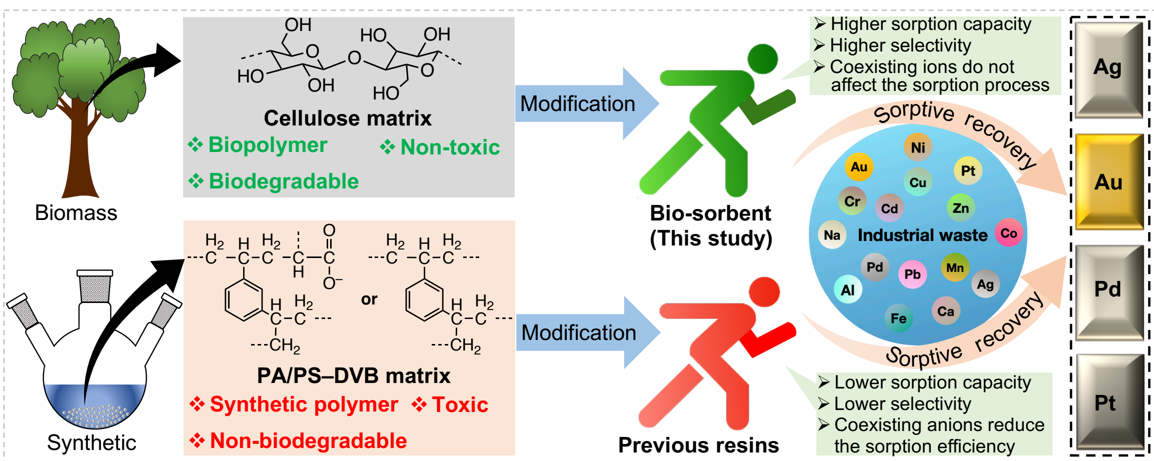
(~99%) over a wide range of pH (< 1 to 6) and high selectivity towards Au^{III} and Pt^{IV} extraction from acidic solutions ([H^+]: ≥ 0.2 mol L^{-1}). The adsorption capacity (mmol g^{-1}; Au^{III}: 5.07, Pt^{IV}: 2.41) and rate to reach equilibrium (≤ 30 min) were significantly higher than most of the reported bio-adsorbents. The Au^{III} or Pt^{IV}, after captured in DMC, was subsequently recovered as Au^0 and Pt^0 (yield > 99%) via incineration. The protocol was verified using real waste samples containing Au^{III} and Pt^{IV} in a mixed matrix of base metal ions, and a quantitative (~100%) and selective extraction of Au^{III} and Pt^{IV} were observed. The proposed post-sorption recovery technique is more effective and straightforward than the typical adsorption-desorption-reduction based method, because of the advantages like no-use of toxic eluents, and no-addition of any reductants to collect the PMs in elemental form.

(b) Recovery of silver and palladium from aqueous matrices



In this study, the biomass-based adsorbent, DMC was used for the selective capture of Ag^I and Pd^{II} from complex aqueous matrices. DMC was found to be an efficient material for the quantitative adsorption of Ag^I, and Pd^{II} from weak to strongly acidic media. The adsorption kinetic data of Ag^I and Pd^{II} were well described by the pseudo-second-order model, and the times required to reach equilibrium were 60 min and 90 min, respectively. The Langmuir isotherm model provided the best fitting for the PM ions adsorption, and the maximum uptake capacities of DMC were evaluated as 10.97 and 4.28 mmol g^{-1} for Ag^{I} and Pd^{II}, respectively. After extraction, the PM ion-loaded DMC was incinerated and the metals were recovered in their pure and elemental form (Ag^0 and Pd^0), with a yield of > 99%. The proposed technique is more straightforward than the typical adsorption-desorption-based recovery method, as employed in commercial operations. Other advantages include process simplicity, high efficiency, non-utilization of toxic eluents, and recovery of the metals in their elemental form without the use of any reductants. Furthermore, the excellent performance (extraction rate: ~99%) of DMC towards the recovery of Ag and Pd from actual waste solutions indicates the potential for the application of the process at a larger scale.

(c) Comparative evaluation of DMC and commercial resins for the recovery of PMs



Herein, a detailed comparative study of bio-sorbent, DMC and synthetic polymer-based commercial resins (Q–10R, Lewatit MonoPlus TP 214, Diaion WA30, and Dowex 1X8) for PM recovery from waste resources was conducted. The performances and applicability of the selected resins were investigated in terms of sorption selectivity, effect of competing anions, sorption isotherms, impact of temperature, and PM extractability from industrial wastes. Although the sorption selectivity toward PMs in acidic solutions by DMC and other resins was comparable, the sorption efficiency of commercial resins was adversely affected by competing anions. The sorption of PMs fitted the Langmuir model for all the studied resins, except Q–10R, which followed the Freundlich model. The maximum sorption capacity of DMC was 2.2 to 42 times higher than those of the resins. Furthermore, the PM extraction performance of DMC from industrial wastes exceeded that of the commercial resins, with a sorption efficiency ≥ 99% and a DMC dosage of 5–40 times lower.

令和３年７月 30 日

学位論文審査報告書（甲）

１．学位論文題目（外国語の場合は和訳を付けること。）

Recovery of Precious Metals from Waste Resources Using Dithiocarbamate-Functionalized Cellulose（ジチオカルバメート修飾セルロースを用いた廃棄物からの貴金属回収）

２．論文提出者　(1) 所　　属　物質化学　専攻

(2) 氏　　名（ふりがな）　Foni Bushon Biswas（フォニ ブション ビスワス）

３．審査結果の要旨（600～650 字）

提出学位論文について、各審査委員が個別に審査した後、令和３年７月８日に予備審査会を実施した。令和３年７月 30 日に行われた口頭発表会に引き続き、審査員による審査委員会を開催し、以下のとおり判定した。

貴金属元素は希少価値が高く先端産業に不可欠な有用元素であることから、高効率なリサイクル技術の開発が求められている。本論文では、ジチオカルバメート修飾セルロース材を用いた固相抽出により、廃液中に含まれる金、銀、白金、パラジウム等を高選択的に回収する新しい分離技術を開発した。一連の研究において、本吸着材は最大吸着量が世界トップクラスであることに加え、強酸性や多量の共存成分が存在する過酷な条件でも貴金属元素を定量的に捕集できることを報告した。また、X 線吸収分析法、X 線光電子分光法等の先端的解析法を駆使して固相表面における錯生成反応等の理論的根拠を明らかにするとともに、産業廃棄物の実廃液を本吸着材に直接通して焼却するというシンプルな化学プロセスで高純度の貴金属元素を 99％以上の効率で回収できることを実証した。

以上、本研究は、廃液中の貴金属元素回収に応用可能な卓越した吸着分離技術を開発したものであり、環境化学およびリサイクル工学の分野において学術的な貢献が期待される。従って、本論文は博士（学術）の学位に値するものと判断する。

４．審査結果　(1) 判　　定（いずれかに○印）　○合　格　・　不合格

(2) 授与学位　博　士（学術）