Dissertation Abstract

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

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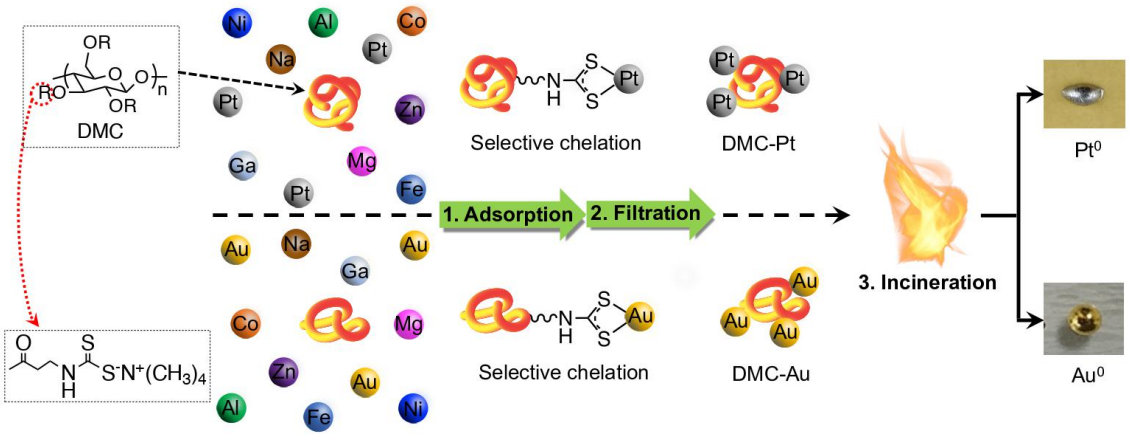
Abstract

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 metal ions. Hence it was expected to have a better selectivity and adsorption capacity of dithiocarbamate-modified cellulose (DMC) to capture soft acid PM ions. Based on the above-mentioned 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.

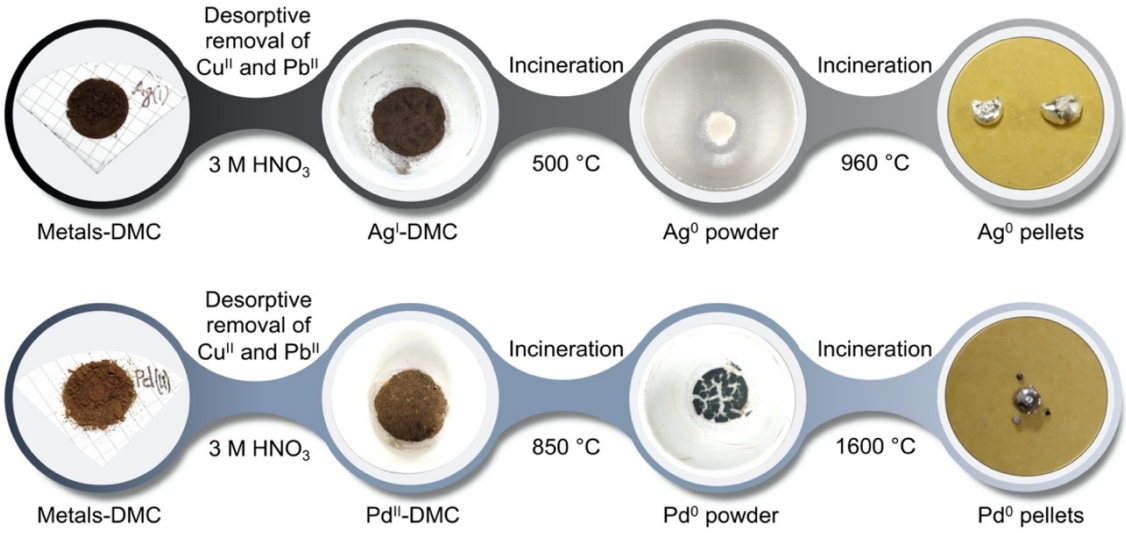
(a) Recovery of gold and platinum from aqueous matrices



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.

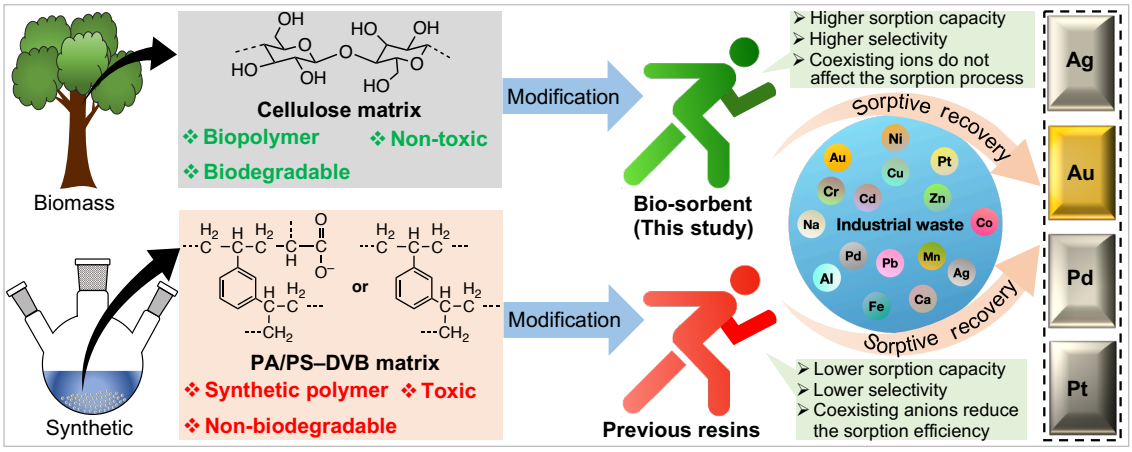
(b) Recovery of silver and palladium from aqueous matrices



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.