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Gold recovery using porphyrin-based polymer from electronic wastes: Gold desorption and adsorbent regeneration

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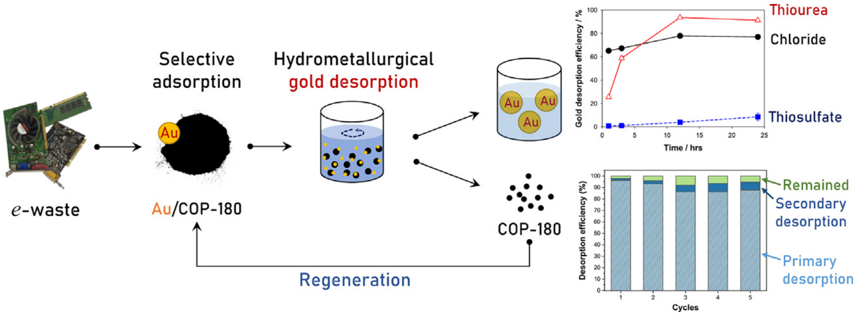
HIGHLIGHTS

- Acid thiourea was well-suited for gold desorption from a porphyrin-based adsorbent.
- High desorption efficiency over 97% was achieved without typical aiding agents.
- Both ionic and metallic forms of gold were simultaneously desorbed in thiourea.
- Gold desorption efficiency maintains up to 94% after five regeneration cycles.
- Rigid binding of gold on the adsorbent affects adsorption capacity, yet negligibly.

GRAPHICAL ABSTRACT



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ABSTRACT

Electronic wastes containing precious metals have great potential as a sustainable source of such metals. Separation and refining, however, remain complicated, and none of the existing technologies have yet experienced commercialization. A novel porphyrin-based porous polymer, named COP-180, was recently introduced as a powerful adsorbent option, especially for gold, and in this study, aspects of desorption and recovery of adsorbed gold and regeneration of the polymer were investigated. A hydrometallurgical method using non-cyanide leaching agents was developed, and an acid thiourea-based solution was found to be particularly suited for the method based on COP-180 with gold desorption efficiency of 97%. Fourier-transform infrared spectroscopy spectra demonstrated the unaffected structure of COP-180 after desorption, implying the potential of its reuse. This high desorption efficiency was achieved even without typical aiding agents by means of a formamidine disulfide-mediated route that prevented thiourea consumption, which is considered a major drawback of the otherwise promising reagent. Using this method, the polymer was able to maintain more than 94% desorption efficiency after five times of regeneration. The results suggest that acid thiourea can offer a workable means of recovering gold particularly from the excellent gold-adsorbent of COP-180, and that repeated regeneration is also possible.

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1. Introduction

Electronic wastes (e-waste) are accruing on a massive scale, reaching over 44 million metric tons in 2016, and the amount continues to rise (Balde et al., 2017; Kumar et al., 2017). E-waste, as a type of waste containing hazardous elements, goes through a series of costly processes for the purpose of treatment. More recently, however, its potential value has been recognized and its profitable use has been attempted to be explored (Akcil et al., 2015; Işıldar et al., 2018). It has been reported that e-waste contains up to hundreds ppm of precious metals, an amount even greater than in ores (Cui and Zhang, 2008; Zhang and Xu, 2016). It is therefore plausible that mining precious metals from e-waste offers a future route for obtaining such valuable metals (Işıldar et al., 2019). Gold embedded in e-waste has attracted considerable attention in urban mining due to its high market price (D'Adamo et al., 2019) and its positive impact on the environment (Awasthi and Li, 2019).

To make a pure form of metals, purification and separation, known as refining, are essential. This process of refining, which may require different technologies, is particularly challenging for precious metals due to poor cost-efficiency and their low concentration (Syed, 2012; Xie et al., 2013). Among the refining processes, adsorption is well-suited for gold recovery because of its exceptional selectivity, including at low concentrations (Xie et al., 2013). A range of adsorbents, such as activated carbon, ion exchange resins, carbon nanospheres, and conducting polymers are available (Rascón-Leon et al., 2018), and yet none of these existing materials are sufficiently satisfactory in terms of capacity, selectivity, and cost.

Yavuz et al. (2018) reported a novel porphyrin-based covalent organic polymer (COP) with superb and selective gold adsorption ability. They found that a porous form of the porphyrin polymer, named COP-180, exhibited surpassingly high selectivity and capacity toward gold, even in mixed metal solutions. Though its basic functions and characteristics were revealed, practical aspects, for example, desorption for reuse, have not been addressed. Consequently, in this study, an efficient means of desorption or a method of ascertaining high reusability was explored. To this end, hydrometallurgical reagents were tested and an optimal condition sought.

Leaching is a method of choice in the extraction of gold when using a hydrometallurgical process (Lu and Xu, 2016; Syed, 2006). Cyanide is a preferred reagent because it has good selectivity and stability toward gold. Detrimental environmental impact associated mainly with its extreme toxicity, however, has been increasingly restricting its use (Rascón-Leon et al., 2018; Senanayake, 2004). Consequently, non-cyanide reagents such as halides, thiosulfate, and thiourea have been examined as potential substitutes (Gurung et al., 2013; Senanayake, 2004). In this work, lower toxicity leaching reagents were evaluated to find alternatives to cyanide that are especially well-suited for COP-180. Gold desorption efficiencies using three non-cyanide candidates for the leaching solution were compared by measuring the gold concentration through inductively coupled plasma optical emission spectrometry (ICP-OES). In addition, structure deformations after the desorption were verified by Fourier-transform infrared spectroscopy (FTIR) as part of the process of selecting a proper desorbing agent along with the results of desorption efficiency. The effects of conditions such as reagent concentration, temperature, and gold content on the desorption were then confirmed with the selected reagent. The underlying mechanisms were speculated through the desorption under anaerobic condition in combination with the results of X-ray photoelectron spectroscopy (XPS) analysis. Finally, the reusability of the adsorbent, which is of prime importance with respect to economic feasibility, was confirmed via five consecutive adsorption and desorption cycles.

2. Materials and methods

2.1. Synthesis of COP-180

A porous porphyrin polymer called COP-180 was synthesized according to previous work (Yavuz et al., 2018), that is, the synthesis of monomer, 5, 10, 15, 20-Tetrakis(4nitrophenyl)-21H, 23H-porphyrin ($TNPPH_2$), was followed by a slightly modified version of previous literature (Bettelheim et al., 1987; Yuasa et al., 2004). In brief, 4-nitrobenzaldehyde and acetic anhydride were dissolved in propionic acid, and the solution was refluxed with the addition of pyrrole. Precipitates were filtered, washed with water and methanol, and dried under vacuum. The dark powder was refluxed in pyridine for 1 h and the final product was collected by filtration. Purification of the product was undertaken with acetone by Soxhlet extraction method.

The polymer synthesis was then conducted according to the literature (Chaudhary and Khurana, 2018; Pachter and Kloetzel, 1951) with slight modifications. The synthesized $TNPPH_2$, p-phenylenediamine, and KOH were all added to dry DMF, and this mixture was treated by mixing for 1 h under nitrogen atmosphere. After cooling, the mixture was added into deionized water and the solution stirred for 1 h. Precipitates were collected by filtration and, as above, the purification process was carried out using the Soxhlet method with water and acetone for 1 day each. The final product, COP-180, was collected after drying at 150 °C for 1 day under vacuum.

2.2. Preparation of gold-adsorbed COP-180

A gold solution was prepared by dissolving gold chloride trihydrate ($HAuCl_4{\cdot}3H_2O$, Sigma Aldrich) in deionized water. Gold concentration in the solution was measured by ICP-OES. One gram of polymer was treated with 200 mL of a gold solution for 24 h with vigorous stirring. The mixture was then filtered using a filter system unit (Corning, pore size = 0.22 μm). The filtered polymer was stored in an oven at 50 °C overnight. The dried gold-adsorbed polymer was collected and stored. The concentration of remaining gold in the filtrate was quantified by ICP-OES and compared with the initial concentration to calculate an adsorbed amount of gold in a milligram of adsorbent. A ratio of adsorbed gold on the polymer was calculated as:

$$q = \frac{(C_i - C_f)V}{W} \qquad (1)$$

where q is the ratio of gold over the amount of polymer in g/g, C_i and C_f are the initial and final concentration of gold in mg L^{-1}, V is the volume of gold solution in L, and W is the amount of COP-180 in mg.

2.3. Gold desorption using leaching solutions

Reagent grade hydrochloric acid (HCl, ≥35%), sodium thiosulfate ($Na_2S_2O_3$), sodium sulfite (Na_2SO_3), thiourea ($CS(NH_2)_2$), and sulfuric acid (H_2SO_4, ≥95%) were purchased from Junsei Chemicals Ltd.. Nitric acid (HNO_3, ≥65%) and disodium phosphate (Na_2HPO_4) were obtained from Samchun Chemicals Ltd.. A mixture of 17% HCl and 8% HNO_3 was prepared for a gold-chloride ligand complex, namely $AuCl_4^-$. A solution of 0.1 M of sodium thiosulfate, 0.1 M of sodium sulfite, and 0.1 M of disodium phosphate was prepared for a gold-thiosulfate-sulfite ligand complex. Thiourea solution was prepared with 0.1 M of sulfuric acid for a gold-thiourea ligand, and the concentration of thiourea was varied (0.1, 0.5, and 1.0 M) (Jing-ying et al., 2012; Syed, 2012).

One hundred milligrams of the gold-adsorbed polymer were added in 100 mL of the leaching solutions mentioned above so that the solid/liquid ratio was maintained to be equal to 1 g L^{-1} in all cases. The ratio of adsorbed gold on the polymer (q) was varied to 0.2, 0.02, and 0.002. The reacted solutions were filtered using a syringe unit (Whatman, pore size = 0.22 μm). The concentration of the leachate was measured by ICP-OES analysis. The percentage of gold desorbed from the polymer was calculated as:

$$Desorption\,(\%) = \frac{C_d \cdot V_d}{Q} \times 100 \qquad (2)$$

where C_d is the gold concentration in the leaching solution (mg L^{-1}), V_d is the volume of the solution (L), and Q is the amount of adsorbed gold on COP-180 in mg.

2.4. Regeneration of adsorbent

Reusability of the adsorbent was evaluated in five consecutive cycles. In each cycle, gold content in the adsorption process was fixed as the q value of 0.2, and a two-step desorption was carried out. For both primary and secondary desorption processes, the gold-adsorbed polymer was treated in a solution containing 0.1 M of thiourea and 0.1 M of sulfuric acid with a solid/liquid ratio of 1 g L^{-1} at 50 °C for 6 h. After the primary desorption, the adsorbent was filtered and dried in an oven. Then the treated adsorbent was re-treated in a fresh acid thiourea solution following the previously described methods to desorb gold left on the polymer. Finally, the adsorbent was filtered and dried for the next adsorption-desorption cycle. The gold desorption efficiency was verified by measuring the gold concentration of each leachate using ICP-OES analysis.

2.5. Analytical methods

Gold concentration in a solution was quantified using inductively coupled plasma optical emission spectrometry (ICP-OES) from Agilent Technologies (5110). The structure of COP-180 was analyzed by Fourier-transform infrared spectroscopy (FTIR) from Thermo Fisher Scientific (Nicolet iS50). X-ray photoelectron spectroscopy (XPS) analysis was performed by Thermo VG Scientific K-alpha. Monochromatic X-ray source Al Kα was used, and binding energies were determined by adjusting the C 1s spectra with an energy of 284.8 eV. The crystalline structures of the adsorbed gold were determined by X-ray diffraction (XRD) with a SmartLab from RIGAKU using Cu Kα radiation (λ = 1.5406 Å) with scattering angles (2θ) of 30–80°.

3. Results and discussions

3.1. Choice of the leaching reagents

Fig. 1 shows the efficiency of gold desorption using different leaching agents, such as mixtures of HCl-HNO_3, thiosulfate-sulfite, and thiourea solutions, after gold was adsorbed on COP-180 with a q value of 0.2. At the beginning of the desorption process, the HCl-HNO_3 solution showed a far higher desorption efficiency (over 60%) than the other solutions. After 12 h of desorption, however, thiourea enabled the release of more than 90% of the gold. During the process, over 70% of the gold was recovered when the HCl-HNO_3 and thiourea solutions were used, while the mixture of thiosulfate and sulfite was found to be inefficient in desorbing gold from COP-180.

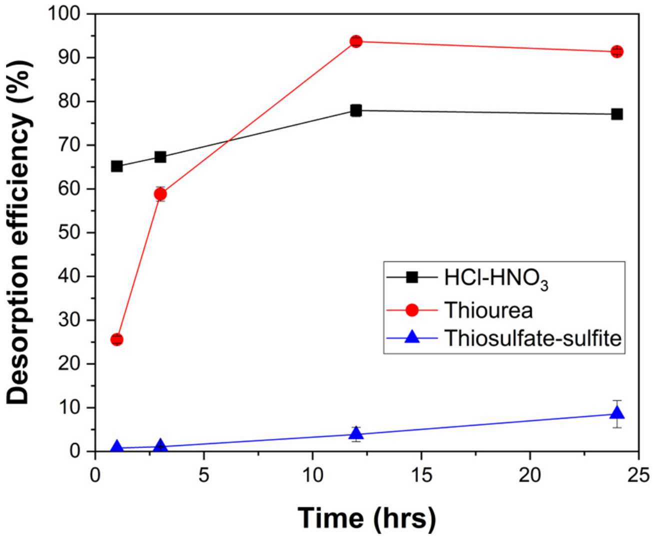

Fig. 1. Gold desorption efficiencies of gold bound COP-180 treated in HCl-HNO_3, thiourea and thiosulfate-sulfite solutions.

Considering the fact that excellent gold desorption efficiencies were obtained using acidic solutions such as HCl-HNO_3 and thiourea rather than thiosulfate-sulfite solution, desorption is facilitated in an acidic condition, which is in line with findings in previous literature (Yavuz et al., 2018), that is, gold is more easily leached from COP-180 at low pH. As the gold ion (Au(III)) appears to combine with the porphyrin head through ionic bonding (Lammer et al., 2015; Zou et al., 2015), it is likely that protons play a role in both processes of gold's attachment to and detachment from the COP-180. That might be the reason for the higher desorption efficiency with the HCl-HNO_3 mixture and thiourea solution. On the other hand, the thiosulfate-sulfite solution, which has to be maintained in an alkaline condition because of solution stability (Syed, 2012), was unsuitable in this specific process. In addition, varied leaching rates and kinetics of the reagents might also play a part; thiourea reacts with gold more rapidly than thiosulfate does (Ding et al., 2019; Li et al., 2018).

The mixture of HCl-HNO_3 led to faster desorption than the thiourea solution at the beginning. This strong acid combination, termed aqua regia, is highly corrosive and oxidative, even at a diluted condition (Hilson and Monhemius, 2006). Upon being mixed with gold, both HCl and HNO_3 rapidly decompose to chlorine and nitric oxide gases, respectively (Xing and Lee, 2017). This rapid nature of the two might be the cause of the high initial desorption rate of gold, though it was not maintained due to its inherently low capacity.

The FTIR spectra of COP-180 show characteristic peaks of the porphyrin structure at 796 cm^{-1} (=C–H bending), 967 cm^{-1} (N–H bending), 1346 cm^{-1} (C=N stretching), and 1596 cm^{-1} (C=C stretching) (Yavuz et al., 2018), and they were identical with the spectra of the gold-adsorbed polymer (Fig. 2). After gold was dissolved in the thiourea solution, the shape of the spectra remained virtually the same as those of COP-180. In contrast, when the HCl-HNO_3 solution was applied, even within 1 h, most of the porphyrin peaks diminished or even disappeared. In this case, the peak of C=O or C–N at 1690 cm^{-1} was observed, confirming the structure modification or disruption of the adsorbent during the treatment. All this leads to the conclusion that thiourea is a well-suited leaching agent for gold desorption in particular from COP-180.

3.2. Effect of desorption reagent concentration, temperature, and gold content

The effects of thiourea concentration and temperature on gold desorption efficiency were tested using 0.1, 0.5, and 1.0 M thiourea

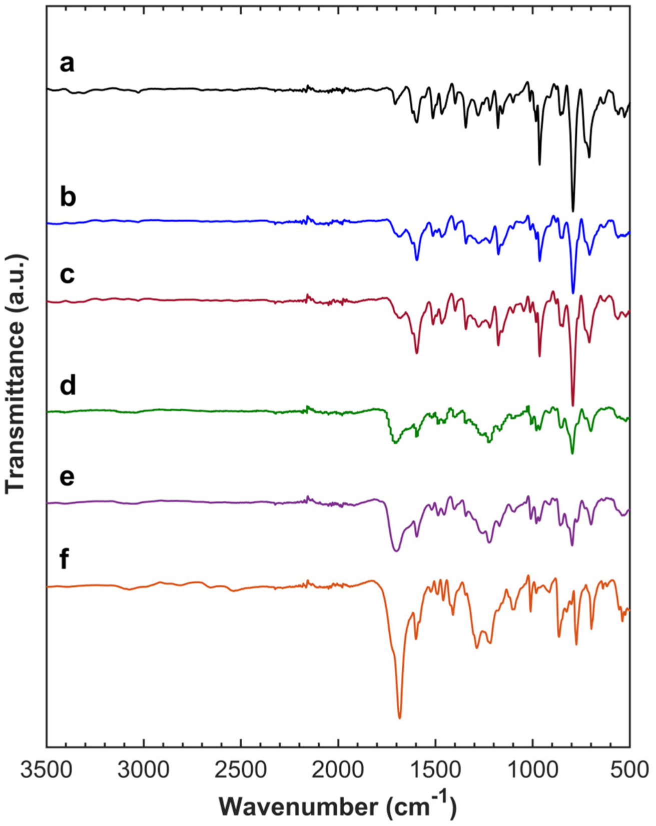

Fig. 2. FTIR spectra of (a) COP-180, (b) Au adsorbed COP-180, (c) COP-180 after gold leaching with thiourea solution for 24 h, (d) COP-180 after gold leaching with chloride mixed solution for 1 h, (e) 3 h, (f) 24 h.

in 0.1 M sulfuric acid as a regenerant, as illustrated in Fig. 3. When the reagent concentration was increased, the rate of gold desorption was concomitantly mounted; and the improvement was even more dramatic when the temperature was raised to 50 °C. Accordingly, the following desorption process employed a treatment condition of 0.1 M of thiourea in 0.1 M sulfuric acid solution at 50 °C.

The desorption efficiency according to the ratio of gold on the polymer (q) is compared, as shown in Fig. 4. The gold content adsorbed on the adsorbent (q) varied from 0.002 to 0.2, and the gold-bound polymer was subjected to desorption in 0.1 M thiourea and sulfuric acid solutions at 50 °C. It was found that desorption efficiency increased with the decrease of gold content: 94% of gold was desorbed when q was equal to 0.02 and the efficiency reached 97% with a q value of 0.002.

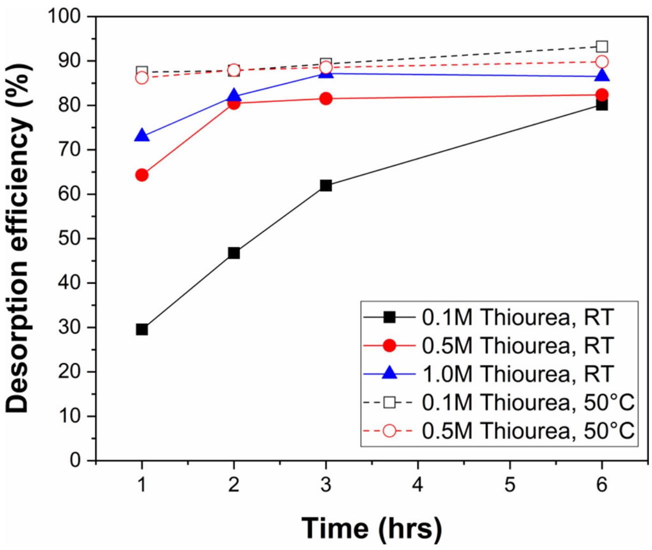

Fig. 3. Gold recovery efficiency in various concentration of thiourea and reaction temperature.

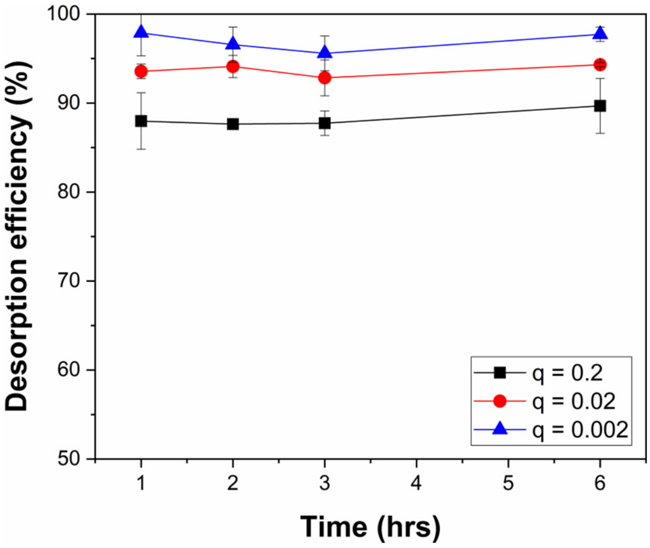

Fig. 4. Gold recovery efficiency in various ratio of gold on the polymer (q).

XPS measurements were performed to unravel gold species adsorbed on the polymer before and after the desorption process. Fig. 5 displays the XPS Au4f region of the adsorbent samples. When gold was adsorbed on the polymer, peaks at 84.4, 85.6, and 88.4 eV (88.1, 89.3, 92.1 eV) were assigned to Au(0) $4f_{5/2}$, Au(I) $4f_{5/2}$, Au(III) $4f_{5/2}$ (Au(0) $4f_{7/2}$, Au(I) $4f_{7/2}$, and Au(III) $4f_{7/2}$), respectively, which correspond to binding energies reported for gold incorporated into the porphyrin core (Fig. 5a and c) (Alonso-Cristobal et al., 2016; Elouarzaki et al., 2014; Müllegger et al., 2011). Regardless of gold content on COP-180, it seems that the adsorbed gold exists in both ionic and metallic forms, as discussed previously (Yavuz et al., 2018). The Au4f peaks disappeared after the desorption with the thiourea solution, especially when a low content of gold was adsorbed on the sample, indicating the successful desorption of gold from COP-180 (Fig. 5d). When the higher amount of gold was adsorbed on the polymer, the desorption caused the proportion of trivalent state (86.3%) of the remaining gold-bound COP-180 to be significantly higher than those of monovalent and metal states, as shown in Fig. 5b. This implies that the ionic form of gold was not fully detached from the polymer structure, whereas the metallic form of gold was in an effective fashion.

The crystallinity of metallic gold was also confirmed by XRD spectra, as shown in Fig. 6. When gold was adsorbed on COP-180, diffraction peaks that matched the JCPDS standard of gold at 2θ angles corresponding to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) were observed, indicating the existence of metallic gold on the polymer (Dong et al., 2016; Tripathy et al., 2013). After the desorption process, the XRD peaks corresponding to metallic gold disappeared or at least were rapidly damped (Fig. 6b and d), confirming the effective dissolution of gold and corresponding with the results of XPS.

3.3. Role of oxygen and formamidine disulfide in desorption

In the case of conventional adsorption/leaching technology, gold leaching processes generally require not only ligands for gold but also oxidants or catalysts, which accelerate the leaching reac-

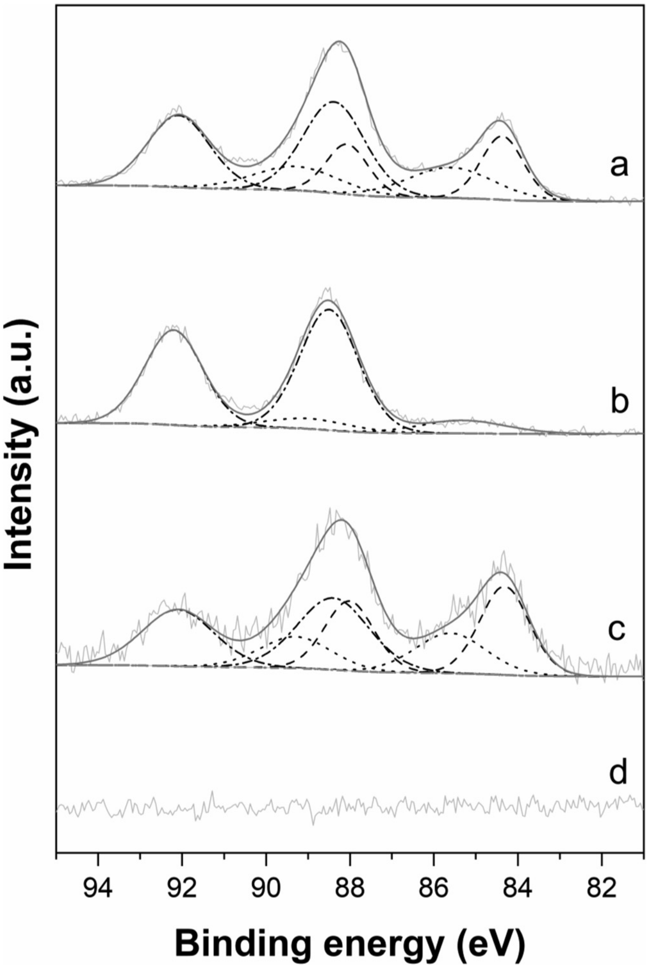

Fig. 5. Au4f core level XPS spectra of (a) gold adsorbed COP-180 with q value of 0.2, (b) COP-180 after desorption of (a), (c) gold adsorbed COP-180 with q value of 0.02, (d) COP-180 after desorption of (c).

tion. For example, thiourea is known to be a good leaching agent particularly in the presence of oxidants such as hydrogen peroxide or ferric ion (Li and Miller, 2006; Olyaei et al., 2019), and the thiosulfate leaching process is facilitated with ammonia and copper (Tamayo et al., 2017; Zhang et al., 2012). To our surprise, however, the exceptionally high efficiency in this study was yielded without such additional reactants. Considering that our experiments were all performed without any such oxidants, the dissolved oxygen was speculated to act as an oxidant.

To verify this speculation, the dissolved oxygen in the solution was removed by purging with nitrogen gas at a rate of 200 cc min^{-1} during desorption in the 0.1 M of the thiourea and sulfuric acid solutions at 50 °C. In the absence of oxygen, the amount of gold dissolved in the solution was found to be quite similar to the value obtained in the presence of oxygen (Fig. 7). For example, when q was 0.2, desorption was indeed slower at the beginning of reaction without oxygen, and yet the final value of dissolved gold after 6 h of reaction was close to the value in the aerobic condition. This implied that the dissolved oxygen in the solution was not the only oxidant in the solution; instead, other compounds with an oxidizing capacity, for example, formamidine disulfide (FDS), which is an oxidized form of thiourea, likely worked as an oxidant during the gold dissolution process (Li and Miller, 2002; Yang et al., 2010). Thiourea could be oxidized to FDS in a reversible way and it could be accelerated with more oxidants added (Marsden and House, 2006). In the absence of such oxidants, it is possible that the oxidation of thiourea was brought about and/or facilitated by the dissolution of ionic gold. The XPS results revealed the co-existence of the ionic and metallic forms of the adsorbed gold on the polymer, implying gold was bound to the adsorbent with three different forms of Au(III), Au(I), and Au(0). In order to dissolve Au(III) ions as a form of ligand complex with thiourea in the aqueous media, it needs to be reduced to Au(I), according to Eqs. (3) and (4). In an anaerobic condition, the oxidation of thiourea can serve as an electron donating half reaction (Eq. (5)).

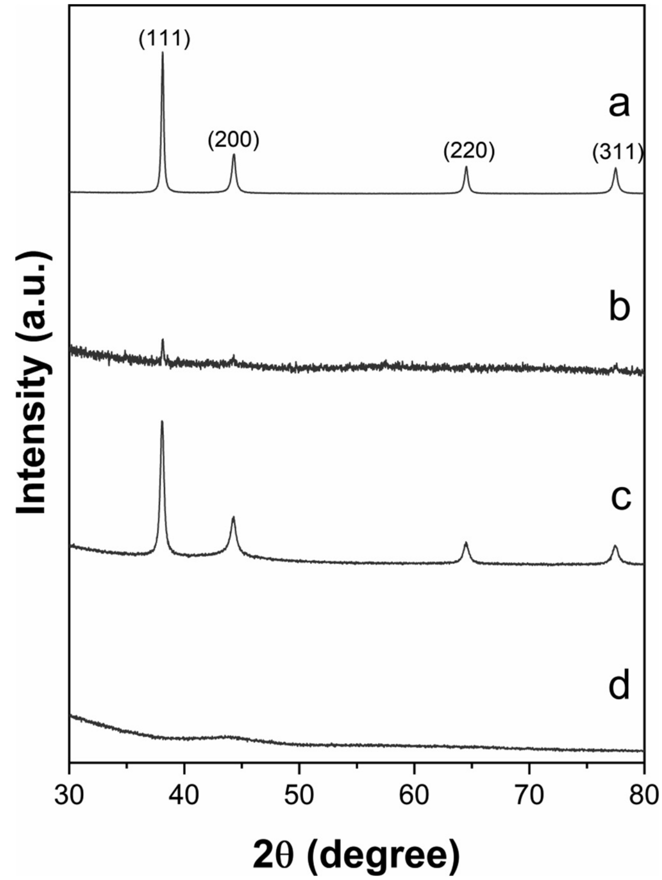

Fig. 6. XRD patterns of (a) gold adsorbed COP-180 with q value of 0.2, (b) COP-180 after desorption of (a), (c) gold adsorbed COP-180 with q value of 0.02, (d) COP-180 after desorption of (c).

$$Au^{3+} + 2e^- \rightarrow Au^+ \tag{3}$$

$$Au^+ + 2CS(NH_2)_2 \rightarrow Au[CS(NH_2)]_2^+ \tag{4}$$

$$2CS(NH_2)_2 \rightarrow NH_2(NH)CSSC(NH)NH_2 + 2H^+ + 2e^- \tag{5}$$

If this happens, then the produced FDS can proceed to oxidize and dissolve Au particles attached on the polymer, thereby increasing the production of the gold ligand complex (Eqs. (6) and (7)).

$$Au^0 + 2CS(NH_2)_2 \rightarrow Au[CS(NH_2)]_2^+ + e^- \tag{6}$$

$$NH_2(NH)CSSC(NH)NH_2 + 2H^+ + 2e^- \rightarrow 2CS(NH_2)_2 \tag{7}$$

All this supports the possibility that the specific adsorption characteristics of COP-180, which is the existence of multiple ionic states of the adsorbed gold, facilitate the desorption of gold with no aiding reagents.

In addition, thiourea can be regenerated from the produced FDS via a reduction reaction, as shown in Eq. (7), and it can in fact serve as a solution to the major concern of using thiourea, namely, con-

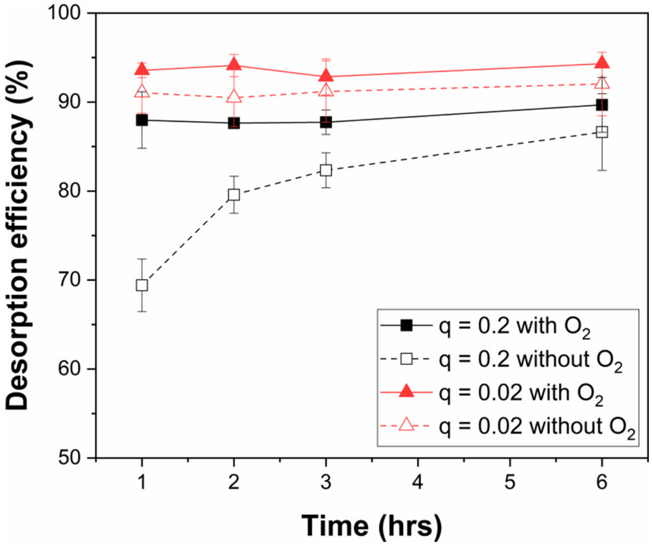

Fig. 7. Comparison in gold recovery efficiency with and without dissolved oxygen in leaching solution.

tinuous consumption. In general, the presence of oxidants causes the further and irreversible oxidation of FDS, leading to the decomposition to cyanamide and elemental sulfur, and thus to the consumption of thiourea and an increase in the cost of the leaching process (Li and Miller, 2002; Olyaei et al., 2019). The desorption from COP-180 was free from this fatal issue. The generated FDS could even be regenerated to thiourea, as it works as an oxidant for oxidizing and dissolving Au particles, limiting the consumption of thiourea. All this suggested that the thiourea solution can indeed be an effective reagent option able to dissolve both ionic and metallic forms of the adsorbed gold.

3.4. Regeneration of adsorbent

COP-180 with the remaining gold after the primary desorption was re-treated with a fresh acid thiourea leaching reagent. As shown in Fig. 8, the desorption efficiency of the remaining gold was kept up to 16.6% during 6 h of reaction time. As an explanation, the rigid and strong chelating effect of the porphyrin structured COP-180 toward gold hindered the further dissolution of Au(III) ions (To et al., 2009), as most of the remaining gold on the polymer after desorption was ionic in form with the oxidation state of + 3, shown in Fig. 5b. Also, the hydrophobic nature of the polymer might disturb the diffusion of thiourea molecules. This undetachable gold portion might negatively impact on the adsorption capacity in the regeneration process.

For the purpose of industrial applications, it is of great importance that adsorption capacity is restored in a cost-effective manner. To prove that repeated regeneration is indeed possible and also to verify how much effect remaining gold has on capacity, a multiple regeneration experiment was executed. In an adsorption process, gold was adsorbed with a q value of 0.2 and two-step desorption processes, that is, primary and secondary desorption in 0.1 M thiourea and sulfuric acid solution at 50 °C, were carried out. The consecutive adsorption and two-step desorption cycles were repeated five times. The gold desorption efficiency of each regeneration cycle is shown in Fig. 9. The total desorption efficiency of the primary and secondary desorption decreased by 6.7% until the third cycle, while in the last two cycles it remained virtually unchanged. This implied that adsorption capacity was impaired by the irreversibly adsorbed gold on the adsorbent by way of lowering the portion of functioning active sites. As already mentioned, it appeared that the strong and rigid binding of gold on the porphyrin structure caused the decrease of adsorption capacity, and yet the occupied capacity was only 5.3% of the adsorbed gold after five regeneration cycles and the desorption efficiency reached more than 94%, showing that the COP polymer has potential for regeneration.

The combined gold recovery process of adsorption and desorption using COP-180 and thiourea was evaluated from an economic point of view, taking account of profits possibly obtained from gold re-sale. The cost of chemical consumption on the polymer synthesis and the desorption were estimated to be $4.83 and $0.43 per gram of COP-180, respectively (Table S1). The cost of energy consumed in both processes was calculated to be $0.13 to treat 1 g of COP-180 (Table S2). Assuming that the average desorption efficiency of gold in a single cycle is 94%, it would cost $28.7 to yield one gram of gold through the whole process. This cost, economically meaningfully cheaper in itself than that of gold (currently

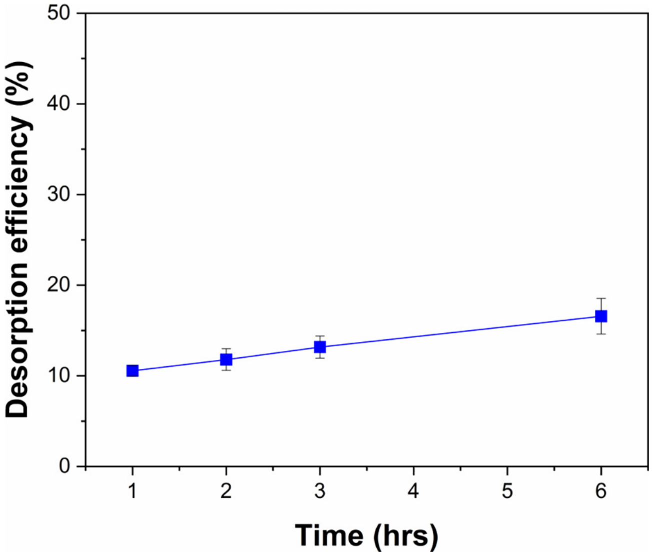

Fig. 8. Gold recovery efficiency of the remained gold on COP-180 by re-treating with fresh thiourea solution.

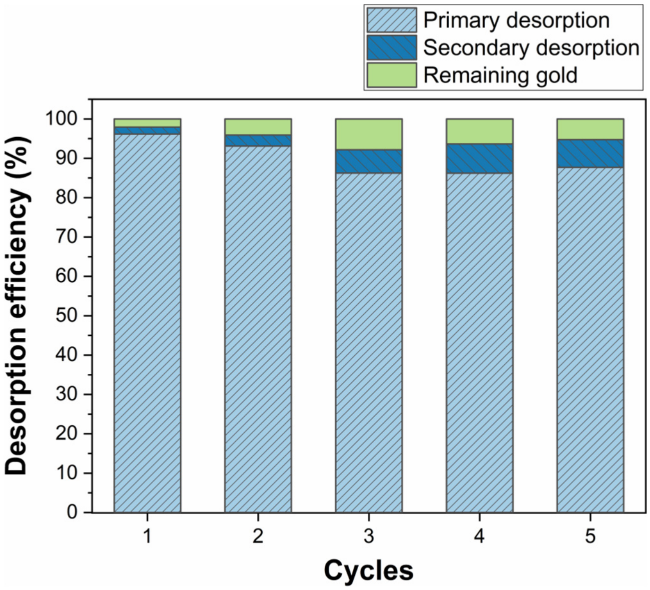

Fig. 9. Desorption efficiency of gold in each regeneration cycle.

$48.33 per gram), would decrease even further: for example, five times of regeneration of COP-180 would lead to a substantially lowered value of $7.95 per gram of gold. Of course, process optimization will be able to maximize profit. It is true that this estimation is very rough, but it appears reasonable to say that it can sufficiently support the sheer potential of our process.

4. Conclusions

In this study, a novel way of gold recovery from electronic wastes was developed by means of employing COP-180 as a particularly powerful gold adsorbent and using an acidic thiourea solution as an effective and yet mild desorption reagent. At an optimal condition, gold leaching efficiency reached up to 97%. This exceedingly high efficiency with no aiding agents was possible because co-existing ionic and metallic gold adsorbed on the polymer worked synergistically together with thiourea, resulting in surpassingly high desorption. Formamidine disulfide, produced from the oxidation of thiourea during the dissolution of ionic gold, appeared to act to oxidize and dissolve metallic gold in the solution. This thiourea-derived oxidant seemed not only to facilitate the simultaneous desorption of ionic and metallic gold but also to prevent thiourea from being consumed, which is distinctively advantageous, as the consumption of reagent is regarded as a major caveat. The reusability of the sorbent using thiourea was confirmed through five consecutive regeneration steps, retaining 94% of desorption efficiency until the last stage. Although the strong and rigid binding of the gold ions on the porphyrin structure in the polymer did impair adsorption capacity, as a small amount of gold was still undetached throughout the regeneration processes, the portion of permanently occupied active sites, which was marginal, remained literally unchanged. The results suggest the thiourea-based method offers a promising desorption approach in particular for gold recovery from the gold-specialized adsorbent, and even more so because of its capability of adsorbent regeneration.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.135405.

References

Akcil, A., Erust, C., Gahan, C.S., Ozgun, M., Sahin, M., Tuncuk, A., 2015. Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixiviants – a review. Waste Manag. 45, 258–271. https://doi.org/10.1016/j.WASMAN.2015.01.017.

Alonso-Cristobal, P., Lopez-Quintela, M.A., Contreras-Caceres, R., Lopez-Cabarcos, E., Rubio-Retama, J., Laurenti, M., 2016. Synthesis of catalytically active gold clusters on the surface of Fe_3O_4 @SiO_2 nanoparticles. RSC Adv. 6, 100614–100622. https://doi.org/10.1039/C6RA20055A.

Awasthi, A.K., Li, J., 2019. Sustainable bioprospecting of electronic waste. Trends Biotechnol. 37, 677–680. https://doi.org/10.1016/j.tibtech.2019.03.004.

Balde, C.P., Forti, V., Gray, V., Kuehr, R., Stegmann, P., 2017. The global e-waste monitor 2017. United Nations University. https://doi.org/10.1016/j.proci.2014.05.148.

Bettelheim, A., White, B.A., Raybuck, S.A., Murray, R.W., 1987. Electrochemical polymerization of amino-, pyrrole-, and hydroxy-substituted tetraphenylporphyrins. Inorg. Chem. 26, 1009–1017. https://doi.org/10.1021/ic00254a011.

Chaudhary, A., Khurana, J.M., 2018. Synthetic routes for phenazines: an overview. Res. Chem. Intermed. 44, 1045–1083. https://doi.org/10.1007/s11164-017-3152-8.

Cui, J., Zhang, L., 2008. Metallurgical recovery of metals from electronic waste: a review. J. Hazard. Mater. 158, 228–256. https://doi.org/10.1016/J.JHAZMAT.2008.02.001.

D'Adamo, I., Ferella, F., Gastaldi, M., Maggiore, F., Rosa, P., Terzi, S., 2019. Towards sustainable recycling processes: Wasted printed circuit boards as a source of economic opportunities. Resour. Conserv. Recycl. 149, 455–467. https://doi.org/10.1016/j.resconrec.2019.06.012.

Ding, Y., Zhang, S., Liu, B., Zheng, H., Chang, C., Ekberg, C., 2019. Recovery of precious metals from electronic waste and spent catalysts: a review. Resour. Conserv. Recycl. 141, 284–298. https://doi.org/10.1016/J.RESCONREC.2018.10.041.

Dong, Z., Liu, J., Yuan, W., Yi, Y., Zhao, L., 2016. Recovery of Au(III) by radiation synthesized aminomethyl pyridine functionalized adsorbents based on cellulose. Chem. Eng. J. 283, 504–513. https://doi.org/10.1016/J.CEJ.2015.07.011.

Elouarzaki, K., Le Goff, A., Holzinger, M., Agnès, C., Duclairoir, F., Putaux, J.-L., Cosnier, S., 2014. From gold porphyrins to gold nanoparticles: catalytic nanomaterials for glucose oxidation. Nanoscale 6, 8556–8560. https://doi.org/10.1039/C4NR02015D.

Gurung, M., Adhikari, B.B., Kawakita, H., Ohto, K., Inoue, K., Alam, S., 2013. Recovery of gold and silver from spent mobile phones by means of acidothiourea leaching followed by adsorption using biosorbent prepared from persimmon tannin. Hydrometallurgy 133, 84–93. https://doi.org/10.1016/J.HYDROMET.2012.12.003.

Hilson, G., Monhemius, A.J., 2006. Alternatives to cyanide in the gold mining industry: what prospects for the future?. J. Clean. Prod. 14, 1158–1167. https://doi.org/10.1016/J.JCLEPRO.2004.09.005.

Işıldar, A., Rene, E.R., van Hullebusch, E.D., Lens, P.N.L., 2018. Electronic waste as a secondary source of critical metals: management and recovery technologies. Resour. Conserv. Recycl. 135, 296–312. https://doi.org/10.1016/J.RESCONREC.2017.07.031.

Işıldar, A., van Hullebusch, E.D., Lenz, M., Du Laing, G., Marra, A., Cesaro, A., Panda, S., Akcil, A., Kucuker, M.A., Kuchta, K., 2019. Biotechnological strategies for the recovery of valuable and critical raw materials from waste electrical and electronic equipment (WEEE) – a review. J. Hazard. Mater. 362, 467–481. https://doi.org/10.1016/j.jhazmat.2018.08.050.

Jing-ying, L., Xiu-li, X., Wen-quan, L., 2012. Thiourea leaching gold and silver from the printed circuit boards of waste mobile phones. Waste Manag. 32, 1209–1212. https://doi.org/10.1016/J.WASMAN.2012.01.026.

Kumar, A., Holuszko, M., Espinosa, D.C.R., 2017. E-waste: an overview on generation, collection, legislation and recycling practices. Resour. Conserv. Recycl. 122, 32–42. https://doi.org/10.1016/J.RESCONREC.2017.01.018.

Lammer, A.D., Cook, M.E., Sessler, J.L., 2015. Synthesis and anti-cancer activities of a water soluble gold(III) porphyrin. J. Porphyr. Phthalocyanines 19, 398–403. https://doi.org/10.1142/S1088424615500236.

Li, H., Eksteen, J., Oraby, E., 2018. Hydrometallurgical recovery of metals from waste printed circuit boards (WPCBs): current status and perspectives – a review. Resour. Conserv. Recycl. 139, 122–139. https://doi.org/10.1016/j.resconrec.2018.08.007.

Li, J., Miller, J., 2002. Reaction kinetics for gold dissolution in acid thiourea solution using formamidine disulfide as oxidant. Hydrometallurgy 63, 215–223. https://doi.org/10.1016/S0304-386X(01)00212-2.

Li, J., Miller, J.D., 2006. A review of gold leaching in acid thiourea solutions. Miner. Process. Extr. Metall. Rev. 27, 177–214. https://doi.org/10.1080/08827500500339315.

Lu, Y., Xu, Z., 2016. Precious metals recovery from waste printed circuit boards: a review for current status and perspective. Resour. Conserv. Recycl. 113, 28–39. https://doi.org/10.1016/J.RESCONREC.2016.05.007.

Marsden, J., House, I., 2006. The chemistry of gold extraction. Soc. Min. Metall. Explor.

Müllegger, S., Schöfberger, W., Rashidi, M., Lengauer, T., Klappenberger, F., Diller, K., Kara, K., Barth, J.V., Rauls, E., Schmidt, W.G., Koch, R., 2011. Preserving charge and oxidation state of Au(III) ions in an agent-functionalized nanocrystal model system. ACS Nano 5, 6480–6486. https://doi.org/10.1021/nn201708c.

Olyaei, Y., Noparast, M., Tonkaboni, S.Z.S., Haghi, H., Amini, A., 2019. Response of low-grade gold ore to cyanidation and thiourea leaching. Part. Sci. Technol. 37, 86–93. https://doi.org/10.1080/02726351.2017.1343881.

Pachter, I.J., Kloetzel, M.C., 1951. The Wohl-Aue Reaction. I. Structure of Benzo [a] phenazine oxides and syntheses of 1, 6-dimethoxyphenazine and 1, 6-dichlorophenazine. J. Am. Chem. Soc. 73, 4958–4961. https://doi.org/10.1021/ja01154a144.

Rascón-Leon, S., Castillo-Ortega, M.M., Santos-Sauceda, I., Munive, G.T., Rodriguez-Felix, D.E., Del Castillo-Castro, T., Encinas, J.C., Valenzuela-García, J.L., Quiroz-Castillo, J.M., García-Gaitan, B., Herrera-Franco, P.J., Alvarez-Sanchez, J., Ramírez, J.Z., Quiroz-Castillo, L.S., 2018. Selective adsorption of gold and silver in bromine solutions by acetate cellulose composite membranes coated with polyaniline or polypyrrole. Polym. Bull. 75, 3241–3265. https://doi.org/10.1007/s00289-017-2206-9.

Senanayake, G., 2004. Gold leaching in non-cyanide lixiviant systems: critical issues on fundamentals and applications. Miner. Eng. 17, 785–801. https://doi.org/10.1016/J.MINENG.2004.01.008.

Syed, S., 2012. Recovery of gold from secondary sources—a review. Hydrometallurgy 115–116, 30–51. https://doi.org/10.1016/J.HYDROMET.2011.12.012.

Syed, S., 2006. A green technology for recovery of gold from non-metallic secondary sources. Hydrometallurgy 82, 48–53. https://doi.org/10.1016/J.HYDROMET.2006.01.004.

Tamayo, J.A., Gómez, S., Calderón, J.A., 2017. Selective electrochemical gold recovery from leaching solutions of thiosulfate. J. Electrochem. Soc. 164, D363–D370. https://doi.org/10.1149/2.0341707jes.

To, Y.F., Sun, R.W.-Y., Chen, Y., Chan, V.S.-F., Yu, W.-Y., Tam, P.K.-H., Che, C.-M., Lin, C.-L.S., 2009. Gold(III) porphyrin complex is more potent than cisplatin in inhibiting growth of nasopharyngeal carcinoma *in vitro* and *in vivo*. Int. J. Cancer 124, 1971–1979. https://doi.org/10.1002/ijc.24130.

Tripathy, S.K., Woo, J.Y., Han, C.-S., 2013. Colorimetric detection of Fe(III) ions using label-free gold nanoparticles and acidic thiourea mixture. Sens. Actuators B Chem. 181, 114–118. https://doi.org/10.1016/J.SNB.2013.01.058.

Xie, F., Fan, Z., Zhang, Q., Luo, Z., 2013. Selective adsorption of Au $^{3+}$ from aqueous solutions using persimmon powder-formaldehyde resin. J. Appl. Polym. Sci. 130, n/a-n/a. https://doi.org/10.1002/app.39521.

Xing, W.D., Lee, M.S., 2017. Leaching of gold and silver from anode slime with a mixture of hydrochloric acid and oxidizing agents. Geosyst. Eng. 20, 216–223. https://doi.org/10.1080/12269328.2017.1278728.

Yang, X., Moats, M.S., Miller, J.D., 2010. The interaction of thiourea and formamidine disulfide in the dissolution of gold in sulfuric acid solutions. Miner. Eng. 23, 698–704. https://doi.org/10.1016/J.MINENG.2010.04.006.

Yavuz, C.T., Hong, Y., Thirion, D., Subramanian, S., 2018. Porous porphyrin polymer and method of recovering precious metal elements using the same. U.S. Patent Application No. 16/212,052.

Yuasa, M., Oyaizu, K., Yamaguchi, A., Kuwakado, M., 2004. Micellar cobaltporphyrin nanorods in alcohols. J. Am. Chem. Soc. 126, 11128–11129. https://doi.org/10.1021/ja0486216.

Zhang, L., Xu, Z., 2016. A review of current progress of recycling technologies for metals from waste electrical and electronic equipment. J. Clean. Prod. 127, 19–36. https://doi.org/10.1016/J.JCLEPRO.2016.04.004.

Zhang, Y., Liu, S., Xie, H., Zeng, X., Li, J., 2012. Current status on leaching precious metals from waste printed circuit boards. Proc. Environ. Sci. 16, 560–568. https://doi.org/10.1016/J.PROENV.2012.10.077.

Zou, T., Lum, C.T., Lok, C.-N., Zhang, J.-J., Che, C.-M., 2015. Chemical biology of anticancer gold(iii) and gold(i) complexes. Chem. Soc. Rev. 44, 8786–8801. https://doi.org/10.1039/C5CS00132C.