Thiourea Leaching: An Update on a Sustainable Approach for Gold Recovery from E-waste

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Abstract

Electronic waste is a dominant global issue with over 50 million tons generated annually. Still, as an amalgamation of precious and rare raw materials, electronic waste is a considerable economic resource with the most valuable components located on the printed circuit boards. Gold is widely used in electronics in numerous applications, although principally for contact points and external connectors. The recovery of gold, due to its high value, is one of the main motivations for recycling e-waste. Although pyrometallurgy and hydrometallurgy processing are still the preferred modes of recovery for gold, the use of high-energy consuming pyro-methods, and the use of gold cyanidation that uses harmful lixiviants are increasingly discouraged. Thiourea has received attention as an alternative lixiviant for gold leaching due to its fast reaction kinetics and less harmful nature. This review aims to provide an up-to-date evaluation of thiourea-gold leaching studies from electronic waste, with emphasis on the recent progression from the classic chemical method to a more sustainable hybrid bioleaching-based system, while its challenges are highlighted. The complementary methods applied for gold retrieval from the pregnant solution are also described with a focus on sustainable methods that have the potential to provide a closed-loop system, the key objective for material recovery in a circular economy.

Graphical Abstract
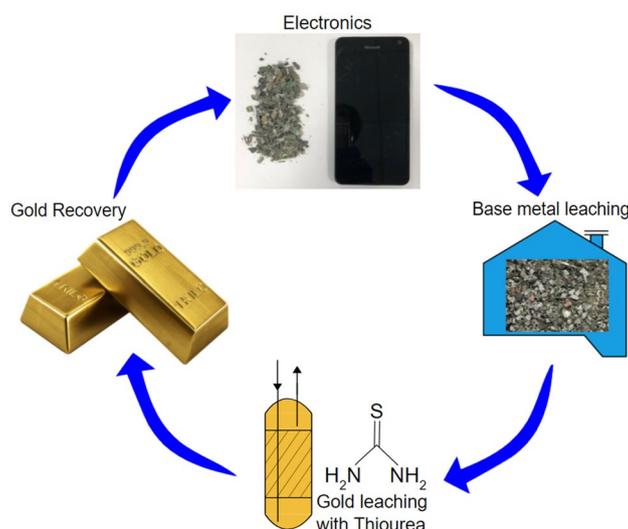
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Introduction

Electronic waste (e-waste) covers all manner of electronic devices from mobile phones and tablets through to the larger appliances such as fridges and washing machines that have ceased to be of value to their users or no longer satisfy their original purpose. The increasing generation of e-waste has led to a major global waste issue. The *Global E-Waste Monitor* reported that in 2019, 53.6 million metric tons of e-waste were generated with projected annual growth of up to 74 million metric tons by the year 2030 [1]. The ever-increasing amount of e-waste if not properly disposed of could have a major detrimental impact on human health and the environment [2]. This has led to many industrialized countries introducing legislation to counteract the rising levels of e-waste and ensure that it is correctly treated locally and sustainably. The transportation and shipping of e-waste worldwide not only incur large costs but also add to the carbon footprint of processes. In 2001, China began implementing legislation that introduced guides for supply chain management and manufacturer responsibilities. Cleaner production and the circular economy were also promoted as part of the legislation in a bid to manage the growing e-waste problem [3]. Japan introduced the Home Appliance Recycling Law (HARL) in 2001 to deal with the increasing generation of waste white goods and waste televisions. It was amended in 2008 to include electronic clothes driers and new LCD TVs [4]. In 2014, the European Union (EU) effected a revised Waste Electrical and Electronic Equipment (WEEE) directive 2012/19/EU that aimed to deal with the increasing generation of e-waste by implementing new targets for reuse and recycling [5].

The environmentally harmful impact of e-waste is not the only motivation for improving end of life treatment. Most e-waste contains an amalgamation of several useful and valuable metals, typically located within the Printed Circuit Board (PCB). Average concentrations of the main metals in a PCB and their corresponding market values are shown as Table 1. Recycling of metals from e-waste is mainly driven by economics, although the large inconsistencies within metal concentrations in different PCBs means valuations are not straightforward. Economics is not the only driver, there are also positive social benefits. In addition, as some natural resources of common elements used in electronic devices such as cobalt, indium, and tantalum have a high supply risk, the finite availability of minerals on earth should be considered [6]. Although iron is the most abundant, many other heavier elements are rarer and their increased usage in new technologies has led to a rapid decrease in known natural deposits. Another issue is highlighted by the elements referred to as 3TG (tantalum, tin, tungsten, and gold), which are known as conflict materials as their mining has been associated with local violence and conflict [7]. As a result, manufacturers are now looking to ethically source their materials due to the negative connotation of mining conflict materials. Altogether, the increasing generation of e-waste should be viewed as an opportunity for secondary sourcing of rare metals.

Common techniques for metal recovery from electronic waste include pyrometallurgy, hydrometallurgy and also, more recently, biohydrometallurgy. Pyrometallurgy includes methods and techniques such as combustion, smelting, and pyrolysis that use high temperatures for metal recovery [14]. Pyrometallurgy methods of metal recovery are employed commercially across Europe with smelting plants in Belgium, Finland, and Sweden [8]. Although these methods result in high yields from the extraction process, there are also many associated disadvantages. The plants not only require high-energy input due to the high temperatures required, but the resulting large emission of toxic gases such as dioxins and polybrominated diphenyl ethers (PBDE) are

Table 1 Average metal concentrations in e-waste [8] and their respective market values, base metal values were originally reported in US $, the exchange rate used was 1.3394 [9–13]

Metal	Average concentration in E-waste (%, w/w)	Value (£ per ton)	Reference
Cu	12–30	7,156	[9]
Zn	0.1–2.5	2,441	[9]
Ni	1–7.2	14,895	[9]
Fe	5–11	69*	[10]
Sn	0.3–3	29,304	[9]
Metal	Average concentration in E-waste (ppm)	Value (£ per kg)	Reference
Au	30–350	44,641	[11]
Ag	80–1000	604	[12]
Pd	30–200	50,895	[13]

*Iron market value is listed as iron ore

detrimental to the environment [15, 16]. In addition, as pyrometallurgy is not very selective in the treatment of metals, the complexity of e-waste often requires further downstream processing of the metal slag [17]. Hydrometallurgy refers to methods that utilize a chemical lixiviant for the dissolution of solid metals into an aqueous phase [18]. Common lixiviants used for metal extraction are usually strong acids or complexing agents, including sulfuric acid, aqua regia, and cyanide. Hydrometallurgy methods produce high yields and can be selective to certain metal groups and comparatively to pyrometallurgy processes, requires less energy input. However, the majority of lixiviants used for metal recovery are toxic and harmful to human health and the environment, with large volumes of chemicals often required for high recovery yields along with additional requirements to ensure safe disposal [19, 20]. In order to adopt a more sustainable approach to metal purification, biohydrometallurgy or bioleaching, a greener, more environmentally friendly method of leaching that utilizes microbial mechanisms for metal recovery, is increasingly being adopted [21].

Gold is used in a number of electronic devices, mainly on connectors and contact points, due to its high electrical conductivity and corrosion resistant properties [22]. With copper being one of the most abundant metals found in e-waste, and gold being one of the most valuable (£44,641 per kg, [11]), research into metal recycling from e-waste has been particularly focused on the recovery of gold and copper. Copper can be leached from e-waste chemically using most lixiviants with high yield and high efficiency, but it can also be leached via the bioleaching mechanisms of redoxolysis and acidolysis [23–25]. Gold in comparison is highly unreactive and requires alternative lixiviants for its recovery. Chemical cyanide is the traditional lixiviant of choice for gold recovery and has been used for gold mining of ores for over 100 years [26, 27] although both biogenic and chemical cyanides have been shown to be an efficient lixiviant for gold recovery [8, 28, 29].

Despite its efficiency in gold recovery, working with cyanide still carries negative connotations. Cyanide is extremely toxic to humans and many other living organisms even at very low concentrations due to its ability to complex with iron (III) and as such to inhibit part of the electron transport chain, a vital part of aerobic respiration [30]. For health and safety reasons, researchers have identified alternative non-cyanide based lixiviants for the recovery of gold from waste electronics, including, thiosulfate species [29, 31, 32], iodine/iodide [33, 34], electrogenerated chlorine [35], ammonium persulfate [36], and thiourea [37–42]. Compared to chemical cyanidation, the alternative processes are less toxic to the user and environment, however, to ensure safe disposal of the lixiviant, post-leaching treatment is often still required. Thiourea leaching of gold from waste electronics has been extensively studied and shows good potential for

industrial application. However, most of the research that considered gold leaching using thiourea focuses predominantly on the leaching steps, but the following recovery stages remain elusive. Transitioning to a circular economy is the focus of many developed nations so a closed-loop approach leading to the recycling of materials as usable products into supply chains is imperative. Recent work by Baniasadi et al. [24] is a demonstration of such a closed-loop approach for copper recycling via bioleaching followed by electrowinning from the leachate. Such a combined approach could be applied to gold recovery from thiourea-gold complex, as numerous methods have been demonstrated including activated carbon [43–45], adsorption [39, 44, 46, 47], cementation [48, 49], and electrowinning [50, 51].

This review aims to assess the current status of thiourea-gold leaching from e-waste combined with the potential methods for recovering gold from a thiourea gold complex. While previous works have reviewed gold-thiourea leaching from primary ores [52], and others have discussed the status of precious metal recovery from PCB and compared thiourea leaching with thiosulfate and cyanide leaching [53], this review will provide an insight into thiourea-gold chemistry and give an update on the status and challenges of leaching gold from e-waste using acid thiourea solutions. It will focus on researcher endeavor to limit the consumption of thiourea while achieving maximal gold recovery. An overview of the diverse recovery methods for the recuperation of gold from the lixiviant will also be assessed for their suitability to provide a closed-loop processing of gold available in e-waste, as required with the global trend of moving from a linear economy to a circular model.

Thiourea Chemistry

Thiourea leaching of gold, despite first being reported in 1941 [54], has never been clearly established into industry. Only a few industrial applications were reported between 1984 and 1992 [52] although more recently, Birloaga et al. [55] report on the development of a pilot plant. The plant, part of the FENIX project, consists of two hydrometallurgical technologies of which, GOLD REC 1, includes an oxidative base metal leaching method combined with thiourea leaching for gold and silver [55]. Despite this limited industrial use, thiourea as a leaching reagent has successfully bridged the transition from primary leaching of ores to gold and silver leaching from secondary sources such as e-waste. The excessive consumption of thiourea, due to its rapid decomposition, is considered one of the main reasons for its lack of industrial application [52]. One of the main challenges for researchers is limiting the decomposition of thiourea in order to ensure the maximum concentration of the active species available for leaching.

Thiourea has been widely investigated for gold recovery from ores [56–58] and more recently the recovery of gold from e-waste. The following section outlines the chemistry of gold leaching using thiourea including competing reactions that can hinder gold dissolution.

Thiourea is soluble in aqueous acidic solutions and with the addition of an oxidant, can solubilize gold, the overall reaction is shown as Eq. 1 [59].
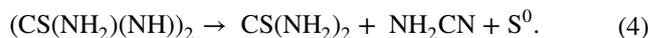
$$Au + 2CS(NH_2)_2 \rightarrow Au[CS(NH_2)_2]_2^+ + e^-. \qquad (1)$$

The Pourbaix diagram for a thiourea system with H_2O_2 oxidant is shown as Fig. 1. This shows the stability of the gold-thiourea complex is dependent on a low pH and a potential between 0.2 V and 0.6 V [60].

The most effective oxidant and conditions for gold leaching were determined to be iron (III) and sulfuric acid, as shown as Eq. 2 [56].

$$Au + 2CS(NH_2)_2 + Fe^{3+} \rightarrow Au[CS((NH_2)_2]_2^+ + Fe^{2+}. \qquad (2)$$

Thiourea readily oxidizes to formamidine disulfide, via a reversible reaction, in the presence of an oxidant. In a system with iron (III), the oxidation of thiourea to formamidine disulfide is shown in Eq. 3. Formamidine disulfide is unstable in acidic conditions and will further decompose, irreversibly, to cyanamide and elemental sulfur, as shown in Eq. 4 [56].

$$2CS(NH_2)_2 + 2Fe^{3+} \leftrightarrow (CS(NH_2)(NH))_2 + 2H^+ + 2Fe^{2+}, \qquad (3)$$

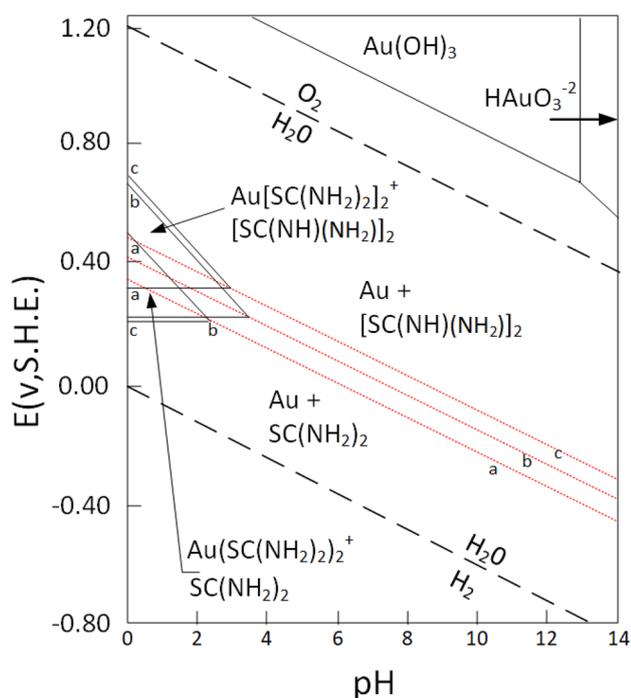$$(CS(NH_2)(NH))_2 \rightarrow CS(NH_2)_2 + NH_2CN + S^0. \qquad (4)$$

The further decomposition of formamidine disulfide to elemental sulfur has been proposed to reduce gold leaching efficiency as the sulfur forms a passivation layer on the gold surface [42]. Loss of thiourea in solution occurs not only via decomposition, but in sulfuric acid systems using iron (III) as the oxidant, thiourea will also react to form an iron sulfate complex as shown in Eq. 5 [61].

$$Fe^{3+} + SO_4^{2-} + CS(NH_2)_2 \rightarrow [FeSO_4(CS(NH_2)_2)]^+. \qquad (5)$$

Two other forms of iron thiourea complexes can also be generated without the addition of sulfate as shown in Eq. 6 and 7 [52].

$$Fe^{3+} + CS(NH_2)_2 \rightarrow [FeCS(NH_2)_2^{3+}, \qquad (6)$$

$$Fe^{3+} + 2CS(NH_2)_2 \rightarrow [Fe(CS(NH_2)_2)_2^{3+}. \qquad (7)$$

The important reactions to note for gold leaching are shown as Eqs. 1 and 2. Equations 3 to 7 show the competing reactions that can occur simultaneously in a gold leaching system using iron (III) and sulfuric acid. The competing reactions hinder gold dissolution by either consuming thiourea or encouraging its oxidation to irreversible products. Although these reactions do occur, the formation constants of Eq. 2 ($log\beta = 21.96$) compared with that of Eq. 5 ($log\beta = 6.64$) (0.13 M thiourea, 0.05 M Fe^{3+}) suggests that the gold complex is less likely to be affected unless excessive concentrations of iron (III) are present [61].

Thiourea Leaching

E-waste Sample Preparation

Electronic waste, in particular PCBs, contains an amalgam of valuable metals, many of which are buried within the board and components. To encourage successful and efficient leaching processes, preparation of the samples is often key. The two most common sample preparation stages used prior to thiourea leaching include particle size reduction and pre-leaching for base metals. With many other elements at higher concentrations, than gold and silver, present in e-waste, the recovery of these metals from mixed metal leachates can be challenging. Particularly as gold is one of the more valuable components and is often a target for recovery.

Fig. 1 Shows the Pourbaix diagram of the gold-thiourea complex in a H_2O_2 system [60]

Particle Size Reduction

Most of the gold used on PCBs can be found exposed at the surface on contact points and connectors as shown in Fig. 2. Chips and components can also contain small amounts of gold that are not visible and often requires liberation to access. Common leaching methods from waste PCBs often employ mechanical crushing stages to reduce particle size as other target metals are located within components.

Despite the surface exposure, the particle size of the waste sample has been reported to affect the recovery of gold. Jingying et al. [38] studied gold-thiourea leaching from unpopulated waste mobile phone PCBs. The effect of particle size was assessed using leaching conditions of 24 g/L thiourea, 0.6% iron (III), pH of 1.00 at 25 °C for a period of two hours. They reported that samples of < 149 μm resulted in around 90% gold recovery compared with around 70% recovery for samples with a particle size of > 149 μm. Similar results were reported by Gurung et al. [39] who studied the recovery of gold using thiourea from waste mobile phone PCBs. They reported that the smaller particle sizes of < 150 μm resulted in 72% gold leaching, particle size between 150 and 300 μm led to 65% gold recovery and particles > 300 μm resulted in only 57% gold recovery. Gurung et al. [39] used leaching conditions of, 0.5 M thiourea, 0.5 M H_2SO_4 at 30 °C for 24 h. Birloaga et al. [40] assessed two different particle sizes (< 3 mm and < 0.1 mm) of waste CPUs (central processing units) using leaching conditions of 20 g/L thiourea, 6 g/L iron (III), and pH 1.4. They reported that gold recovery increased more than fourfold when comparing particle sizes of < 3 mm (18.2% recovery) to < 0.1 mm (82.1% recovery) as shown by Fig. 3. Using the same experimental conditions but using residues obtained following an oxidative leaching process, it was reported that 45% gold dissolution was obtained with a particle size < 3 mm and 90% copper removed. A particle size of < 2 mm with 60% and 75%
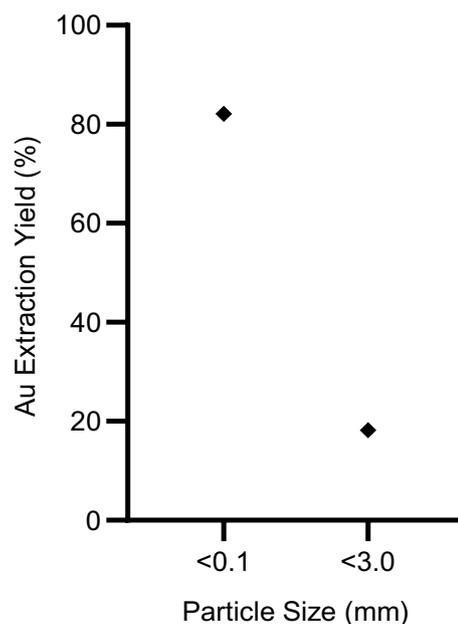

Fig. 3 Effect of particle size on gold extraction from waste CPUs. Adapted from [40]

copper removed resulted in 68% and 69% gold recovery, respectively [40]. The effect of particle size is clearly significant, demonstrating that a smaller particle size is beneficial for maximizing gold recovery. Several authors suggest the reason this improved gold recovery is the resulting increased surface area which leads to increased contact between gold particles and thiourea [38–40].
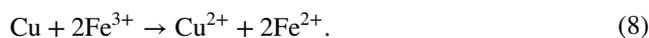
Pre-leaching

Reducing the decomposition of thiourea can be associated with its own issues when used in an iron (III)/sulfuric acid system. Iron (III) can complex with free thiourea, reducing


Fig. 2 Printed Circuit Boards. Gold location is indicated by white arrows; **a** Nokia 3310 PCB, **b** System X telecom PCB, **c** Blackberry PCB
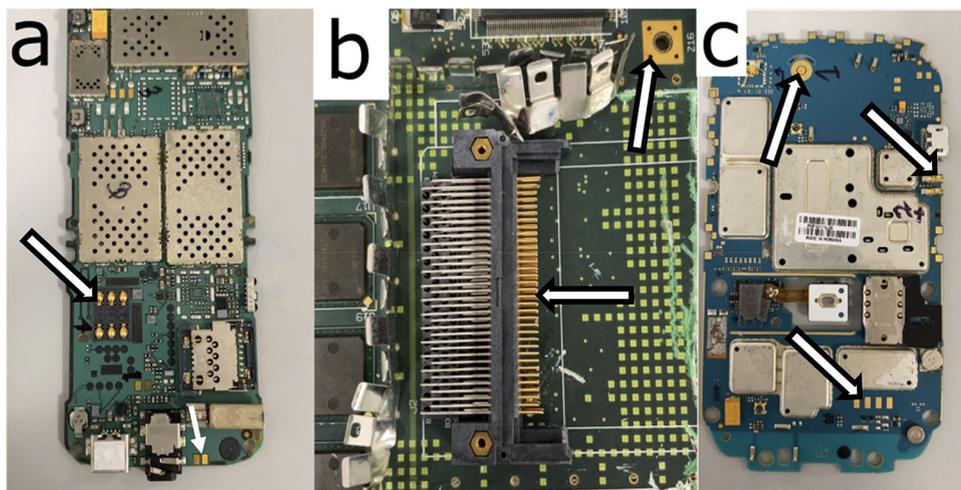
thiourea availability for gold complexing. High concentrations of iron (III) in the system also encourage oxidation of thiourea, which again reduces the concentration available for gold complexing. The application of this system for e-waste introduces more challenges to reduce thiourea decomposition as copper and other base metals are introduced. Copper is a main component of e-waste that on average constitutes up to 30% by weight of the PCB [62]. In the presence of iron (III), copper can be leached via the redox mechanism shown in Eq. 8.

$$Cu + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+}. \tag{8}$$

The leaching of copper via this mechanism reduces the available iron (III) ions required for the thiourea leaching of gold. At high concentrations, copper (II) ions can also cause increased decomposition of thiourea to $[(CS(NH_2)(NH))_2]$ and will form a copper (I) complex as shown in Eq. 9 [41, 63].

$$Cu^{2+} + (n+1)CS(NH_2)_2 \rightarrow Cu(CS(NH_2)_2)_n^+ + (CS(NH_2)(NH_2)^+)_2. \tag{9}$$
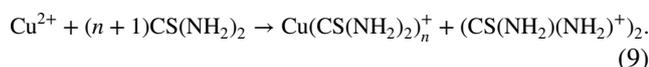
Calla-Choque et al. [64] studied the effect of different metallic ions on thiourea stability. They reported that high concentrations of copper (II) ions caused increased thiourea decomposition due to the redox potential rising above 0.5 V, a point where thiourea is readily oxidized to formamidine disulfide. In order to limit this effect and improve gold leaching efficiencies, the use of an oxidative pre-leaching step to remove copper and other base metals from the sample has been reported [25, 40–42, 65, 66]. Birloaga et al. [40] used a pre-leaching stage of 2 M H_2SO_4 and 20 ml H_2O_2 (30 wt%) at 30 °C for three hours prior to thiourea leaching. This first step resulted in 76% copper removal, while over 90% of the copper was removed following a second pre-leaching treatment using the same conditions. Thiourea leaching was completed on crushed waste PCB samples by thiourea leaching using a solution of 20 g/L thiourea, 6 g/L iron (III), and 10 g/L sulfuric acid with a 1/10 s/l (solid/liquid) ratio. They reported that whereas no gold dissolution occurred when the sample did not undergo any pretreatment, up to 82% gold recovery was achieved following pretreatment [40]. In further studies completed by Birloaga et al. [41], a similar effect was observed when leaching gold from a sample of gold pins from a PCB that contained high concentrations of copper. Behnamfard et al. [65] also used an oxidative pre-leaching stage of 100 ml 2 M H_2SO_4, 25 ml 35% H_2O_2 on 12 g of crushed PCB with a particle size of < 300 µm. No comment was made on the effect of gold dissolution without the pre-leaching stage; however, the authors reported that > 84% gold was recovered after pre-leaching. Torres and Lapidus [66] assessed multiple
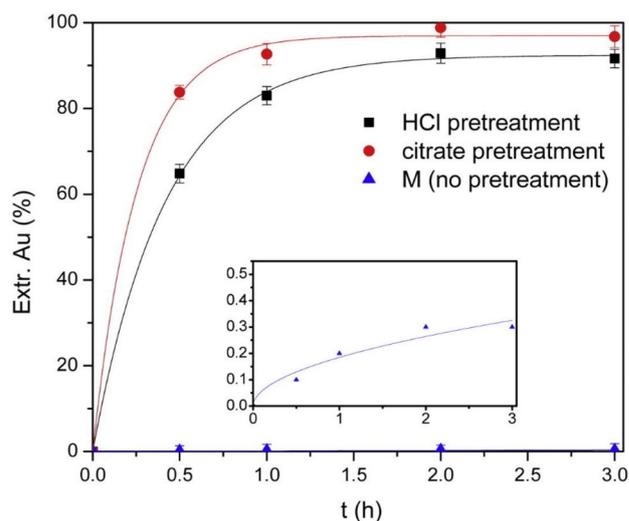
Fig. 4 Gold leaching using thiourea (0.4 M thiourea, pH 1.5, 3 h) following pretreatment using HCl and Citrate and no pretreatment, M. Reprinted with perimission from [66]

Table 2 Reagent concentrations and copper extraction yields obtained in the counter-current leaching process (total volume 250 ml, 15% pulp density, room temperature, 1-h leaching time, 200 rpm agitation speed) [25]

Reagent concentrations	Copper extraction yield (%)
3 M H_2SO_4 & 20% (V/V) H_2O_2 (30% wt/vol)	~ 100
2 M H_2SO_4 & 20% (V/V) H_2O_2 (30% wt/vol)	~ 100
1.7 M H_2SO_4 & 17% (V/V) H_2O_2 (30% wt/vol)	> 98

pre-leaching mechanisms using electronic waste PCBs, comparing inorganic acids of HCl, HNO_3, and H_2SO_4 to organic carboxylates in EDTA and citrate. They assessed gold recovery using thiourea following either pretreatment routes of (1) HCl pretreatment assisted with sparging and (2) citrate with hydrogen peroxide pretreatment. The authors report that after one-hour leaching time, 83% of gold was extracted following route (1) and 93% following route (2). As shown by Fig. 4, in the same time period, less than 0.5% gold was extracted without the use of any pretreatment [66].

Although the addition of a pre-leaching stage increases the chemical usage, it has been shown to be a useful step to improve gold recovery. Birloaga and Vegliò [25] used a counter-current oxidative leaching process with an aim of reducing reagent consumption. The counter-current leaching method shows that a reduction of reagent concentrations, as shown in Table 2, still results in sufficient copper extraction suitable for downstream leaching of gold using thiourea. Bioleaching or bio-oxidation for copper dissolution prior to

gold recovery instead of chemical pre-leaching could be a viable green alternative.

Gold Leaching Conditions

Pyper and Hendrix [67] suggested the rate of gold leaching is dependent on both thiourea and oxidant concentration as well as the pH. Many researchers adjust the thiourea concentration, leaching time, temperature, and oxidant concentration to optimize gold recovery. The optimal conditions determined in the relevant studies are summarized in Table 3 and is discussed in the following.

Lee et al. [37] studied the leaching of gold, silver, and copper simultaneously from integrated circuits (ICs) from waste PCBs using thiourea. They studied the effect of thiourea concentration, iron (III) concentration, temperature, and leaching time. Thiourea concentration was tested over the range of 2.5 g/L and 100 g/L. The optimal thiourea concentration was determined to be 70 g/L, used in a system with 13 g/L iron (III), 1.8 M H_2SO_4 at ambient temperature, and over a leaching time of seven hours. These conditions resulted in 100% gold recovery. Lower thiourea concentrations were shown to have lower recovery, which could be due to the competing reaction with the other ions present in the sample. Higher concentrations also resulted in lower gold recovery, possibly due to an increased decomposition of thiourea to formamidine disulfide and then irreversibly to cyanamide and elemental sulfur (Eqs. 3 and 4).

Jing-ying et al. [38] also reported that higher concentrations of thiourea in a leaching system with iron (III) resulted in lower leaching rates over time due to the decomposition of thiourea. The researchers tested thiourea concentrations of 20 g/L, 24 g/L, and 28 g/L. The highest gold recovery of 89.67% was obtained using 24 g/L of thiourea with a leaching time of 2 h, 6 g/L iron (III) at pH 1.0. Camelino et al. [42] also measured gold leaching using the same conditions (2 h, 6 g/L iron (III), pH 1.0) while varying the thiourea concentration (20 g/L, 24 g/L, 28 g/L). Maximum recovered gold was determined to be 39% at 24 g/L thiourea concentration. A 5% pulp density was used in the study by Camelino et al. [42], compared with 1.25% used by Jing-ying et al.

[38]. An improved leaching efficiency was also observed at lower pulp densities by Gurung et al. [39]. The effect of the oxidant (iron (III)) concentration was also assessed by Jing-ying et al. [38] at concentrations of 2 g/L, 4 g/L, and 6 g/L in a system of 24 g/L thiourea at pH 1.0. The lower iron (III) concentrations resulted in lower gold recoveries, highlighting the important role the oxidant plays in the dissolution of gold using thiourea. The authors do also suggest that there is a balance between not limiting the gold leaching reaction with low oxidant concentrations, as shown by the 2 g/L and 4 g/L experiments but to also avoid using excess oxidant as this may increase the thiourea decomposition.

With a view to improve the process efficiency and reduce the consumption of reagents, Gurung et al. [39] studied several variables to determine the optimum leaching conditions. The agitation speed was assessed from 150 to 500 rpm, this was shown to have no effect on the gold recovery, and for efficiency, therefore, 150 rpm was chosen as optimal condition. Temperature of the system was also assessed and 45 °C determined to be the optimum. The authors reported that the reaction was suppressed at 60 °C suggesting that the higher temperature catalyzed the decomposition of thiourea by iron (III). A similar effect was also shown by Lee et al. [37] as their system showed decreased gold leaching rates at both 40 °C and 60 °C. Birloaga et al. [40] also reported on a decrease in gold leaching efficiency at temperatures above ambient.

Gurung et al. [39] determined the optimum thiourea and acid concentration against the pulp density, ranging from 2.85 to 20.0 mg/ml. Thiourea concentration was varied from 0.03 M to 1 M with an increase in gold recovery as the thiourea concentration increases. The best recoveries (> 70%) were obtained at the lowest pulp density (2.85 mg/ml) using the highest thiourea concentration, 0.5 M and 1 M. No improvement was shown when using the highest concentration (1 M) and with the aim to reduce reagent consumption the ideal thiourea concentration was chosen as 0.5 M. Acid (H_2SO_4) concentration was assessed from 0.01 to 1 M. The experiments using the lowest pulp density (2.85 mg/ml) again reported the best gold recovery (> 70%) although no change can be observed between the different acid

Table 3 Optimal values for thiourea-gold leaching from e-waste under acidic conditions. *Pulp density was not reported in the referenced material

| Thiourea concentration (g/L)	Oxidant Fe(III) concentration (g/L)	Acidity–H_2SO_4, (concentration or pH)	Temperature (°C)	Leaching time (h)	Gold recovery (%)	Pulp density (g/L)	Reference
70	13	1.8 M	Ambient	7	100	10	[37]
24	6	pH 1.0	25	2	90	-*	[38]
38.06	0.5	0.05 M	45	2	90	2.85	[39]
20	6	pH 1.4	Ambient	3.5	82	10	[40]
24	6	pH 1.0	Ambient	2	39	50	[42]

concentrations. At higher pulp densities, it can be observed that no increase in gold recovery occurs using acid concentrations stronger than 0.05 M. The reported optimum concentration was chosen as 0.05 M [39]. Unlike similar studies where the authors determine the optimal oxidant concentration, Gurung et al. [39] measured the effect of the addition and omission of an external oxidant (iron (III)) against gold recovery. They reported that the addition of 0.01 M iron (III) resulted in maximum gold recovery being achieved after 2 h leaching compared with the same concentration of gold leached after 6 h in the absence of iron (III). It is suggested that the slower leaching rate observed in the experiments without external iron (III) was catalyzed by the iron present from the sample. It was also observed that > 0.01 M iron (III) caused a decrease in the gold leaching efficiency, as suggested by Jing-ying et al. [38] the excess oxidant concentration may cause the increased decomposition of thiourea and limiting the gold recovery.

Hybrid Thiourea Bioleaching

There are three mechanisms of biohydrometallurgy, acidolysis, redoxolysis, and complexolysis. Acidolysis is the generation of biogenic acid, and complexolysis refers to biogenic production of complexing agents. With regard to bioleaching processes, the most common biogenic acid is produced via the oxidation of elemental sulfur to sulfuric acid as shown in Eq. 10 [68].

$$S^0 + 1.5O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-}. \tag{10}$$
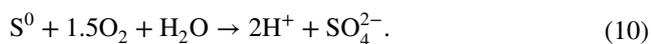
Redoxolysis refers to the bacterial oxidation of iron (II) to iron (III) as shown in Eq. 11, and the reduction of zero valence metals (M^0) with iron (III) as shown in Eq. 12 [69].

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O, \tag{11}$$

$$M^0 + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+}. \tag{12}$$
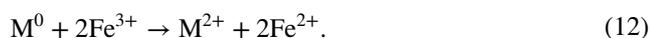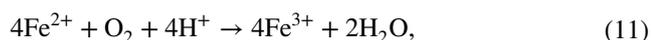
The redoxolysis mechanism provides an opportunity to combine chemical thiourea leaching with biogenic production of the iron (III) oxidant into a hybrid bioleaching method as shown in Fig. 5. Guo et al. [70] coupled bacterial oxidation of iron (II) with thiourea leaching in a two-step leaching process of gold from a refractory gold concentrate. This was employed as a bio-oxidation pretreatment and resulted in 95% gold recovery compared with 92% recovery in a single step with chemical iron (III) and not with biogenic iron (III) [70].

The first use of the combined thiourea bioleaching system was reported by Rizki et al. [71]. They developed the hybrid system using iron-oxidizing archaea and thiourea for application on waste PCBs. They aimed to reduce thiourea
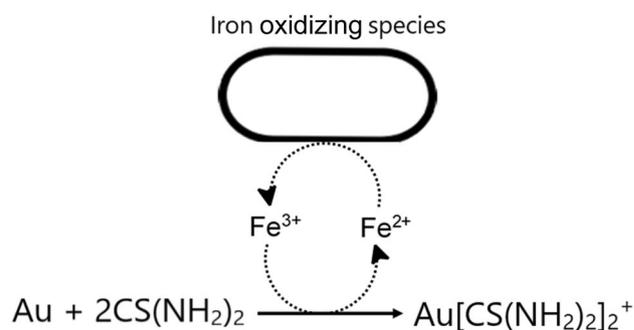
Fig. 5 Combined biohydrometallurgy method for gold leaching using thiourea

consumption and control Eh for maximum gold recovery. Initially, two iron-oxidizing strains of bacteria and four iron-oxidizing strains of archaea were assessed for thiourea tolerance, concluding that the archaea species *Acidiplasma sp* Fv-AP was best suited for the hybrid system. It showed good thiourea tolerance at 25 mM and is moderately thermophilic (45 °C) reducing the risk of additional thiourea decomposition due to higher temperatures. It was reported that the best gold recovery was obtained using 1 mM iron (III) with 10 mM of thiourea and a starting pH of 1.5. Utilizing the bacterial oxidation of iron (II) allowed Rizki et al. [71] to manipulate the redox potential and maintain it between 490 and 545 mV (E_H vs SHE), resulting in up to 98% gold dissolution. They also assessed the effect of sodium sulfite (Na_2SO_3) an antioxidant that was previously reported to shorten the gold extraction length and decrease thiourea consumption [72]. Rizki et al. [71] reported that although the addition of sodium sulfite to the leaching system did not improve the gold recovery, the remaining thiourea in solution was 6.8 mM, compared to 1.6 mM without the sodium sulfite. Since the introduction of antioxidants to reduce thiourea consumption would add an extra cost to the process, an economic assessment of costs incurred from the antioxidant addition against the cost saved by the reduction in thiourea consumption should be completed to determine any viable use in the future.

Gold Recovery from Thiourea Solutions

In order to make a successful transition to more sustainable methods, the recovery of metals from a leachate needs to also be sustainable. Often recovery methods require the use of low flash point solvents, excessive heat, and therefore, energy or large volumes of harmful chemicals. These methods can also be time consuming and require multiple, complicated steps to reach the final product. On the other hand, recovery methods such as cementation or electrowinning, which have been reported to produce metals in high degree

of purity generally do not require many steps to obtain the desired product [24, 73].

Adsorption

Due to the relatively low concentration of gold within electronic waste, pre-concentration steps can be required to obtain concentrated gold solutions for further processing. To this aim, several methods can be used including activated carbon [43–45] ion exchange resins [74] and organic adsorbents [39, 44, 46, 47]. Commercial activated carbon, which is typically produced from coconut shells, becomes activated after burning as oxygen interacts with the external C–C bonds creating adsorption sites [43]. It is a good adsorbent for gold solutions as it is stable at high temperatures and, in both acid and alkali conditions [75]. However, its use in a thiourea leaching system can be challenging due to competing adsorption from other metallic species, adsorption of excess thiourea and the post adsorption recovery of gold [43]. In addition, without pre-leaching, the presence of copper in e-waste can have a significant negative effect on gold loading. Zhang et al. [45] reported that even at low concentrations of copper (II) (100 mg/L) the rate and capacity for gold loading was reduced due to competitive adsorption. Other carbonaceous materials have been assessed for gold adsorption, including Nakbanpote et al. [44] who reported the use of rice husk ash, a common waste product from the agricultural sector in Thailand. They also studied the adsorption properties of heat immobilized *Chlorella vulgaris* a microalga. Fourier transform infrared spectroscopy (FTIR) showed functional groups of carboxylates, ketones, and esters as the active sites for adsorption on *C. vulgaris*. Rice husk ash spectra revealed carboxylate, ketone, and siloxane groups. The adsorption mechanism was proposed as covalent bonds from the lone pair of electrons on the oxygen from the active sites. Activated carbon showed that the best adsorption capacity at 35.88 mg Au/g, 28.22 mg Au/g was reported for rice husk ash with 10.34 mg Au/g reported for *C. vulgaris*. The three reported materials require a heat treatment of > 300 °C to be activated prior to use which could be unsustainable and uneconomic on a larger scale. Côrtes et al. [47] studied the gold-thiourea adsorption properties of chitin extracted from shrimp. They obtained > 80% gold adsorption after precipitation of other substances using sodium hydroxide. The chitin was reported to have a capacity of 58 mg Au/g. Gurung et al. [39] reports on the use of a crosslinked persimmon tannin gel (CPT) and compares adsorption of gold-thiourea with activated carbon. The CPT gel was shown to have better selectivity compared to activated carbon with less base metal adsorption although activated carbon showed greater capacity for gold at lower adsorbent density as shown in Fig. 6.
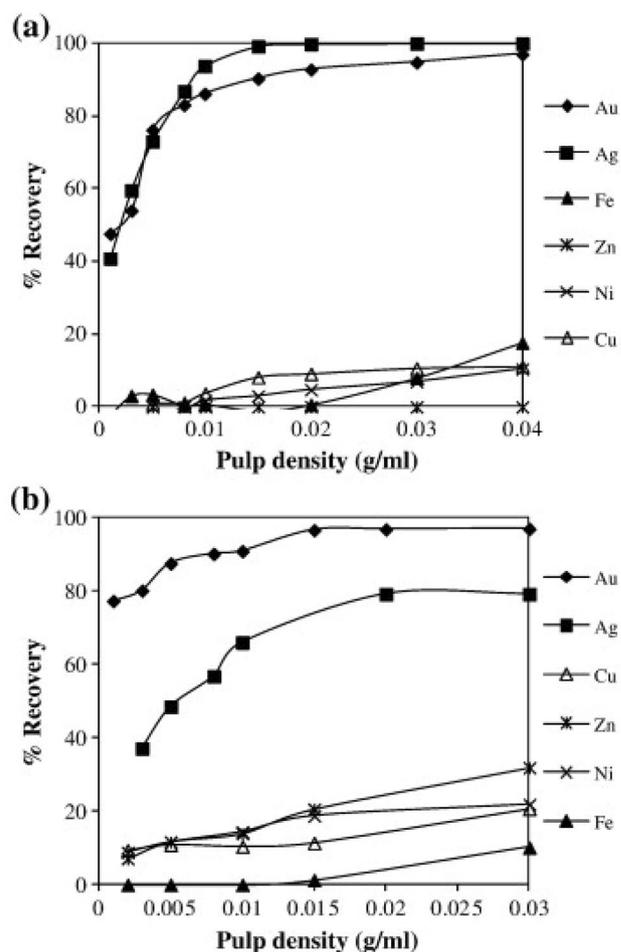
Fig. 6 Adsorption of gold and other metals from acid thiourea leachate by using **a** crosslinked persimmon tannin gel (CPT gel) and **b** activated charcoal. Reprinted with permission from [39]
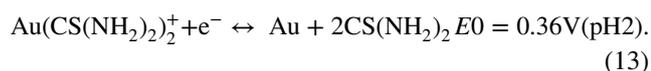
Rather than the gold-thiourea complex adsorbing onto the CPT, elemental gold was shown to have reduced onto the gel. The reduction is suggested to be caused by phenolic hydroxyl groups adjacent to the adsorbed species. Adsorption methods are typically used to concentrate the metals in solution ready for further processing by electrowinning, therefore, requiring that the metals be desorbed from the adsorber. The authors suggest the recovery of gold from CPT gel should be done by incineration since the gold is already in elemental form and the biomass can be incinerated easily [39]. Incineration of biomasses to recover gold is feasible. However similar to pyrometallurgy methods for recovery, the use of high temperatures alongside a resulting large carbon footprint from the emissions is unfavorable in today's climate and energy crisis. Removal of gold from the adsorbents can be done by elution with other lixiviants. Nakbanpote et al. [44] used sodium thiosulfate ($Na_2S_2O_3$) for this purpose. Gold-thiosulfate has a higher formation constant (log $\beta = 26$) compared to gold-thiourea (log

β = 21.95) meaning that as the thiosulfate passes over the adsorbed gold, ligand exchange reactions occur giving rise to the gold-thiosulfate complex [76]. The elution of the new complex occurs due to the change in charge from the positive gold-thiourea [Au(CS(NH$_2$)$_2$)$_2$$^+$] to the negative gold-thiosulfate [Au(S$_2$O$_3$)$^-$] complex. As the adsorption is suggested to be reliant on the positively charged gold-thiourea complex, covalently bonding with the lone pairs of electrons, the change in charge frees the gold and allows elution [44]. Adsorption methods can be useful for concentrating gold leached from e-waste. However, the general selectivity of adsorbents could restrict its use without the addition of a pre-leaching step. Application of suitable elutants is also important to ensure that elution is not restricted to incineration or the use of more harmful chemicals.
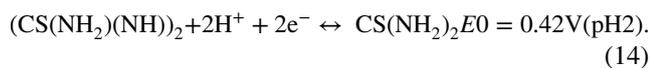
Electrowinning

Electrowinning is the process of depositing a metal via reduction onto a cathode from a leachate using an electrical current. Hydrometallurgy methods of metal recovery from e-waste often results in a mixed metal leachate containing several metal species that can be electrowon such as copper, nickel, zinc, and gold. The reduction potential of a metal species determines the ease of which it will be electrowon from solution. If species with similar reduction potentials exist in the same solution, selective electrowinning becomes problematic, particularly in the case of e-waste leaching.

Electrowinning cells can vary in design from simple tanks containing multiple anodes and cathodes, to split cells where the anode and cathode are separated by an ion exchange membrane. The reduction of gold-thiourea occurs via the reaction shown in Eq. 13 [77, 78].

$$\text{Au(CS(NH}_2)_2)_2^+ + e^- \leftrightarrow \text{Au} + 2\text{CS(NH}_2)_2 \quad E0 = 0.36\text{V(pH2)}. \tag{13}$$
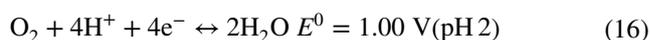
In a thiourea leachate, many other competing reactions can also occur during electrowinning. When using an excess of thiourea, formamidine disulfide is also generated (Eq. 3), this can be reduced back to thiourea at the cathode causing passivation onto the gold surface, as shown by Eq. 14 [50].

$$(\text{CS(NH}_2)(\text{NH}))_2 + 2\text{H}^+ + 2e^- \leftrightarrow \text{CS(NH}_2)_2 \quad E0 = 0.42\text{V(pH2)}. \tag{14}$$

Acidic conditions are used for thiourea leaching and can, therefore, result in hydrogen evolution competing at the cathode as shown in Eq. 15 [78]. Oxygen reduction at the cathode is always a competing reaction during electrowinning but often goes unnoticed due to the higher concentrations of metals in comparison to dissolved oxygen [78]. Low concentrations of gold from the leaching of e-waste can cause the oxygen reduction to become more dominant

in the electrowinning system hindering the gold deposition. Oxygen is reduced via the reaction shown in Eq. 16 [50, 78].

$$2\text{H}^+ + 2e^- \leftrightarrow \text{H}_2 \quad E^0 = -0.10 \text{ V(pH 2)}, \tag{15}$$

$$\text{O}_2 + 4\text{H}^+ + 4e^- \leftrightarrow 2\text{H}_2\text{O} \quad E^0 = 1.00 \text{ V(pH 2)} \tag{16}$$

As mentioned above, one method to concentrate or isolate the gold and avoid competing reactions when electrowinning is enriching the leachate by using activated carbon, ion exchange resins, or a natural adsorbent. Conradie et al. [74] used simultaneous electrowinning after eluting gold from an ion exchange resin (Minix) using an acidic thiourea solution. The experiments were completed using a cathode box, containing two cathodes and three anodes, whereby the eluant from the resin was passed directly through the box and recirculated back through the resin. Different cathode materials were tested for efficiency and corrosion resistance from the solution. Granular carbon cathodes resulted in adsorption of thiourea leading to reduced process efficiency, and steel wool was also unsuitable as the authors reported that the corrosive nature of the eluant caused decomposition of the cathode. Stainless steel mesh and wool showed good corrosion resistance, but the mesh was preferred over the wool based on ease of recovering the gold from the cathode material. Higher flow rates through the electrowinning cell resulted in better current efficiencies, 100% current efficiency was achieved using a current density of 50A/m^2, cathode area of 60cm^2, gold inlet concentration of between 1330 and 1410 ppm, and a linear flow velocity of 50 mm/min. Higher gold concentrations also lead to better current efficiencies demonstrating that the gold deposition is mass transfer controlled [74]. Urbanski et al. [51] also studied electrowinning of gold from the gold-thiourea complex based on typical eluants obtained from stripping activated carbon. They generated synthetic eluants with a composition of 6 g/L thiourea, 45 mg/L gold, and 20%v/v isopropanol all acidified to a pH of 1.2–1.6 using sulfuric acid. The gold was solubilized by the addition of a small excess of 30% hydrogen peroxide. The addition of isopropanol is suggested to limit the oxidation of thiourea at the anode. Limiting the thiourea oxidation at the anode is imperative as the generation of formamidine disulfide can cause passivation on the gold surface when reduced at the cathode [77]. Further anodic oxidation can lead to the generation of elemental sulfur which again can also passivate the gold surface. The authors suggest using a split cell where the cathode and anode are separated by an exchange membrane to reduce this effect. Urbanski et al. [51] assessed the effect of temperature on plating recoveries and showed that 100% gold was recovered from the plating cell using a platinum mesh cathode at 60 °C. Current efficiencies were measured against time at 60 °C at various current densities (0.08, 0.10, 0.12, and 0.20 A/dm^{-2}). The

peak current efficiency (8%) was obtained after 10 min at 0.12 A/dm^{-2}. The current efficiency dropped sharply as time passed and the higher current density also produced lower current efficiencies while achieving 100% gold recovery. The lower current efficiencies were attributed to the competing reactions at the cathode as shown in Eq. 16. Similar obser-

Precipitation

Awadalla and Ritcey [80] used a solution containing 40% sodium hydroxide and 12% sodium borohydride balanced with water (VenMet solution), sodium borohydride (SBH) being the reducing agent. The reduction of gold from the thiourea complex is shown as Eq. 17 [80].

$$8Au[CS(NH_2)_2]_2^+ + BH_4^- + H_2O \rightarrow 8Au + 16CS(NH_2)_2 + BO_2^- + H^+. \tag{17}$$
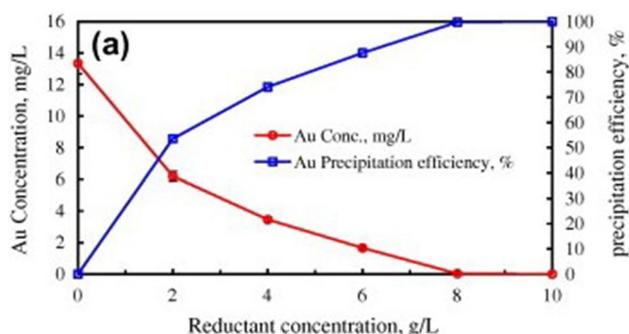
vations were made in the work by Juarez and Dutra [50] as an increase in current density resulted in lower current efficiencies. Increasing the gold-thiourea concentration was shown to improve the current efficiency. Cathodic polarization curves completed by Juarez and Dutra [50] show that higher plating temperatures are also favorable for gold reduction. It also highlighted from the cathodic polarization curves that gold reduction from the gold-thiourea complex is preferential over the reduction of formamidine disulfide. Ippolito et al. [79] more recently studied gold electrowinning from thiourea solutions obtained from the leaching of high-grade e-waste. Using graphite electrodes, 95% gold was recovered after 1.5 h of plating at low current intensity of 75 mA. Similar to other studies, the current efficiency was low at only 4.06%. The authors also commented on the increase (> 10%) of thiourea regeneration via formamidine disulfide reduction at the anode.

These studies demonstrate the effectiveness of using electrowinning as the recovery method for gold from acidic thiourea solutions. To ensure that the electrowinning process is efficient, it should be noted that high gold concentrations are favorable. Gold concentrations from e-waste leaching can be too low for efficient electrowinning from thiourea solutions. Adsorption methods (Sect. 3.1) should be considered before electrowinning as a way of increasing the gold concentration in the leachate. Sufficient mixing of the solution is also important as the reaction is mass transfer controlled. Higher temperatures up to 60 °C can reduce the potential required for gold reduction, and higher current densities can cause competing reactions to become dominant and hinder gold deposition via passivation. Cathode material selection is also important to ensure efficient recovery of gold. Due to the acidic nature of the thiourea solution, selection of a corrosion resistant material is crucial. Increased surface area using a wool can improve process efficiencies, but challenges of product removal from the cathode should be considered.

Reduction using SBH is typically carried out in the pH range of 5–7 as pH < 5 causes hydrolysis of the reducing agent. Despite this, the authors demonstrate that borohydride reduction is efficient in acidic pH from 1.5 to 3.0 although large excesses of SBH were required for the most acidic pH of 1.5. Complete reduction of 10 ppm of Au was achieved using SBH in a molar ratio of 2.5 / moles of Au after 2 min at room temperature. The effect of SBH reduction was also tested in the presence of other metallic species. Zinc and silver ions had positive effects on reduction efficiency whereas other metal ions interfered (Fe, Cu, Ni, Co). Stepwise addition of SBH was shown to limit the interference from other metallic ions. Single-step addition using a molar ratio of 12.5 SBH/Au recovered > 98% gold with a purity of 57%. Two-stage addition of 9.375 SBH/Au followed by 3.125 SBH/Au resulted in > 89% recovery after the first step; however, the purity obtained was significantly higher at > 83%. After complete reduction of gold, the free thiourea concentration was analyzed and was shown to be unchanged allowing the thiourea to be recycled for other leaching experiments [80]. Behnamfard et al. [65] also used SBH to precipitate gold from acid thiourea solutions. The authors assessed varying concentrations of the reducing agent from 2 to 10 g/L. Figure 7 shows the relationship between dissolved gold concentration and reductant concentration. At > 8 g/L SBH, 100% gold
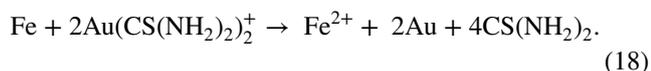

Fig. 7 Concentration of gold in solution after precipitation with different amounts of SBH as a reducing agent and the resulting precipitation efficiency. Reprinted with permission from [65]

precipitation was achieved. No comment was made on the purity of the precipitated product; however, the reduction in other metal species reported in the post-precipitation leachate suggests that the metals were co-precipitated. The potential to recycle thiourea is an advantage of using SBH, and boron is environmentally toxic. Ensuring maximum gold recovery requires high concentrations to be used, future work should focus on reducing SBH consumption and recycling it using an enclosed system to reduce any excess release of boron compounds into the environment.

Cementation

Cementation refers to the displacement of metal ions from solution using more reactive metal species [48]. The use of zinc dust for cementation from gold cyanide solutions is an established industrial method known as the Merrill-Crowe process [81]. Several metal species have been shown to be useful cementing agents for gold from thiourea solutions including, copper, zinc, nickel, aluminum, and iron [41, 82]. Birloaga et al. [41] reported successful gold recovery using zinc and copper powders in 2 M sulfuric acid solutions, iron powder was also tested, but gold was still present in solution. Copper was also used by Gurung et al. [39] and yielded > 80% gold regardless of copper pulp density (1–9 mg/ml). Copper was chosen as the reduction agent as to avoid base metal precipitation because copper has the closest reduction potential to gold as shown in Table 4 [39].

Wang et al. [49] investigated the effect of iron (III) ions on gold cementation from thiourea solutions using iron powder. The reaction for gold cementation using iron is shown as Eq. 18 [49].

$$Fe + 2Au(CS(NH_2)_2)_2^+ \rightarrow Fe^{2+} + 2Au + 4CS(NH_2)_2. \tag{18}$$
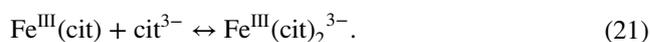
Iron (III) is the most common used oxidant for leaching with thiourea, and it was observed through preliminary experiments that iron (III) had a negative effect on reduction efficiency. Redox potentials of systems with varying concentrations of iron (III) were measured as cementation experiments progressed. Increasing the concentration of iron (III) increases the redox potential which the authors suggest that it leads to

the solubilization of iron powder using iron (III) the reaction of which is shown as Eq. 19 [49].

$$2Fe^{3+} + Fe \rightarrow 3Fe^{2+}. \tag{19}$$

To limit the effects of iron (III), the authors added tri-sodium citrate as a complexing agent to produce iron (III) citrate. The reactions of iron (III) and citrate (cit) are shown as Eqs. 20 and 21 [83].

$$Fe^{3+} + cit^{3-} \leftrightarrow Fe^{III}(cit), \tag{20}$$

$$Fe^{III}(cit) + cit^{3-} \leftrightarrow Fe^{III}(cit)_2^{3-}. \tag{21}$$

The benefit of adding citrate was shown as > 95% gold recovery was obtained after 30 min in conditions containing the maximum tested iron (III) concentration of 0.03 M and 0.2 M of citrate. Without the presence of citrate, 0.02 M of iron (III) only yielded > 60% current efficiency. There was no mention of thiourea stability after gold reduction, but this simple addition of tri-sodium citrate was shown to benefit gold reduction in the presence of iron (III). Utilizing this method for e-waste leachates could be sustainable if the recovery of both thiourea and iron (III) can be employed. Simple filtration was employed most often post-cementation to recover the gold product; however, no comment was made by authors regarding separation of any excess reducing agent. Washing of the filtrate with a different gold solution is a reported method for removing residual reducing agent as it is displaced by the gold [81]. Sulfuric acid washing to solubilize excess reducing agent is also a popular option. Minimizing the remaining reducing agent is important when factoring in the purity of the gold, excessive amounts could devalue the product.

Electroless nickel immersion gold (ENIG) is a common process used in PCB manufacturing to protect electrical contact points from galvanic corrosion [84]. Typical immersion gold baths contain potassium dicyanoaurate and as previously mentioned, ongoing social and environmental concerns are leading researchers to move away from cyanide species. Son et al. [85] have proposed the use of a gold-thiourea bath in replacement of this. Corrosion resistance is an important quality for immersion gold coatings, so bath composition was determined based on the corrosion properties of the deposit. Gold concentration and temperature accelerated the deposition of gold by lowering the activation energy; pH and thiourea concentration showed no effect. Tafel curves showed that the best corrosion resistant deposit was obtained from a bath containing 0.1 M thiourea, 0.1 M sulfuric acid, and 150 ppm of gold at 80 °C [85]. The composition of the gold-thiourea immersion baths may be difficult to obtain directly from leaching e-waste. Many electrical products have varying concentrations of gold, obtaining

Table 4 Oxidation Reduction potentials of metals utilized as cementing agents for gold from Thiourea complexes (vs SHE)

Metal	Oxidation reduction potential (V)
Zn	− 0.76
Fe	− 0.44
Ni	− 0.26
Pb	− 0.13
Cu	+ 0.34

a concentration suitable for immersion plating may incur additional steps. E-waste also contains a complex mixture of multiple elements that can often interfere with extraction and recovery processes. The use of adsorption methods to separate the gold species from the mixture could be a useful stage to implement prior to electroless plating in a closed-loop system. The work completed by Son et al. [85] demonstrates the viability of using gold-thiourea baths for ENIG processes. Another alternative lixiviant in thiosulfate was assessed for immersion plating by Son et al. [85]. The thiourea baths produced coatings that are marginally better than those produced from gold-thiosulfate baths in terms of corrosion resistance, deposition rate and morphology.

Conclusion

As an alternative to gold cyanidation, thiourea has shown to be an effective lixiviant. In comparison to aqua regia and cyanide, the thiourea system is less toxic to the environment and user. When leaching gold from e-waste, prior removal of base metals should be considered to help limit the oxidation of thiourea to formamidine disulfide. Oxidative leaching using a combination of sulfuric acid and hydrogen peroxide is a common method employed for base metal removal, but if used industrially, complete base metal removal would require large volumes of harmful chemicals to be used, which would need to be treated prior to disposal. Although adding an additional step, the selective leaching of gold and silver, which is achieved using thiourea, becomes more efficient in the absence of base metals. As a sustainable alternative, the use of biogenic lixiviants for base metal removal is being considered increasingly. For a circular economy model of material recycling aiming for zero waste, the use of iron and sulfur-oxidizing bacteria can be used by regenerating the lixiviant. Tighter control over the leaching conditions would also be beneficial, maintaining a low redox potential and limiting oxidant concentration. The hybrid leaching system involving iron-oxidizing bacteria also shows great potential. Utilizing the microbial recycling of iron (III) oxidant in a closed-loop system offers a way of limiting oxidant concentration, therefore, helping to reduce the thiourea consumption. Recovery of the gold from the thiourea complex is possible using common techniques; however, low gold concentrations could lead to increased steps. Efficient recovery is key when striving for sustainable methods, and low gold concentration can lead to reduced efficiency when electrowinning. Adsorption methods show good gold recovery; however, the most commonly used activated carbon is challenging for selectivity. Pre-leaching samples, particularly for e-waste, may provide another benefit to prevent competing adsorption reactions as well as competing electrowinning reactions. Sustainable materials such as rice husk and biomass have shown to be suitable adsorbents for the gold-thiourea complex. Reusing waste materials from other sectors is also an important asset, especially as part of a global circular economy. Industrial use of electrowinning should be considered, although capital costs for specialized flow cells or split cells may warrant cementation to be more economical particularly if the reducing agent used can be recycled. Closed-loop systems, where little to zero waste is generated, should be the future for industrial material recovery. Further research into the recyclability and reuse of thiourea after gold recovery should be completed as to also fit in with this model. The products from thiourea decomposition, if reuse cannot be achieved could also be used in other sectors. If the elemental sulfur can be isolated, its use in sulfur-oxidizing bioleaching systems could increase thiourea's appeal as a leaching agent although this is another area for further research. Bio-recovery, which promotes the use of microorganisms, is a suitable technology to support this idea, and the inclusion of iron-oxidizing bacteria as part of the thiourea-leaching system is a successful example of such a sustainable bio-recovery process that can demonstrate its adoption for industrial use.

Declarations

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