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From trash to resource: a green approach to noble-metals dissolution and recovery

Abstract: A process based on the lixiviant properties of organic mixtures of dihalogen/S,S-ligands, N,N'-dimethylperhydrodiazepine-2,3-dithione (Me_2dazdt) and tetraalkylthiuramdisulphide (Et_4TDS) in the presence of diiodine, for gold recovery from the non-ferrous metal fraction of real shredded waste electric and electronic equipment (WEEE), is presented here. Selective dissolution of metals is achieved through a sequence of three steps where the oxidation of different kinds of metals is achieved by using: (1) refluxing water solutions of HCl 1:5 under Ar atmosphere (Sn, Zn, etc.); (2) water solutions of $\text{NH}_3/(\text{NH}_4)_2\text{SO}_4$ mixtures in the presence of H_2O_2 on the resting sample (Cu, Ag); and (3) acetone solutions of Me_2dazdt or $\text{Et}_4\text{TDS}/\text{I}_2$ mixtures on the final residue (Au). Each step is followed by a further treatment for: (1) metal recovery, in the case of Au, Cu, Ag; and (2) inertization, in the case of heavy metals. As a whole, the process is very promising for effective recovery of gold and other valuable noble-metals and for using non harmful reagents in mild conditions.

Keywords: gold; leaching; PCBs; recycling; WEEE.

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1 Introduction

In order to balance sustainability with economic development, most countries are promoting new strategies on waste management to face the increasing demand on the

planet's limited resources. The goal is to create value from waste, including reuse, recycling, waste-to-energy and recovery without endangering human health and without using processes or methods that could harm the environment. Coordination chemistry may help to provide suitable tools for metal recovery by waste, as done in the past by ores using hydrometallurgical methods. Remarkably, waste may contain precious and other strategic metals [1] in amounts comparable or even higher than in their ores, as happens in the case of e-waste such as printed circuits boards (PCB) or other hi-tech scraps, thus called "urban mines".

Leaching is the primary process in hydrometallurgy whereby the metal values of a solid metal-bearing material are transferred into an aqueous solution by the action of a lixiviant. A variety of hydrometallurgical procedures has been proposed in the past by several authors for the dissolution/extraction of Noble-Metals (NMs) [2–4]. The most significant approaches are generally based on the following two processes: (1) cyanidation based on the use of cyanide salts into basic media with subsequent adsorption on activated carbon and reduction of the complex by electro-winning. This is still the most widely used process for gold and silver extraction from ores, despite the toxicity of cyanides; and (2) unselective dissolution of NM by strong and oxidizing acids, generally based on the use of aqua regia, the well known 3:1 mixture of hydrochloric and nitric acids followed by recovery of the NM^{n+} cations from the solution by selective extraction with suitable reagents. These procedures, conventionally employed for jewelry ashes or for refining NMs slags, are carried out in at least two steps and use hazardous substances (the high aggressive aqua regia produces toxic fumes, e.g., NO_x).

Alternative reagents, such as thiourea or thiosulfate [5], have been proposed for gold etching, but they have not found large-scale applications, mainly due to the large consumption of non-recyclable reagents. As a further example, mixtures of thionyl chloride and organic solvents/reagents such as pyridine, N,N-dimethylformamide and imidazole, named organic aqua-regia, have aroused great interest in their capability to dissolve gold and other noble metals with high dissolution rates under mild conditions [6]. This method was applied for etching Au metallization on

a circuit board. Changing the organic reagent and reaction conditions, the proposed mixtures selectively dissolve gold and palladium at high rates and room temperature and pressure. These features were taken as unique when compared to other etching reagents, and ascribed to the formation of donor-acceptor adducts between thionyl-chloride and the solvent/reagent, which provide an enhanced reactivity to organic aqua-regia reagents. However the harmful nature of employed reagents/solvents, which are not recyclable, makes this formulation not fully appealing for large scale applications [7].

Despite these methods being effective, new challenges for green chemists are being addressed to find novel strategies in order to couple effectiveness with sustainability.

With the view to finding more sustainable reagents for recovery of NMs, we have thoroughly investigated the etching properties of dihalogen adducts of cyclic-dithiooxamides in organic solvents. These non-cytotoxic reagents have been shown to be very effective in dissolving elemental palladium and gold in a one-step reaction and under mild conditions [8–12]. Depending on the nature of the cyclic-dithiooxamide, its mixture with diiodine is capable to dissolve even platinum [13].

Satisfactory results for lab-scale practical applications have been obtained by using this class of reagents for palladium recovery from spent three way catalysts [14, 15] as well as for gold recovery from selected waste from electric and electronic equipment (WEEE) [16] and from deprocessing procedures for the failure analysis of micro-electronic devices [17, 18]. Selective and almost quantitative dissolution and recovery of the metal from a complex matrix has been reached. Recently, diiodine mixtures with ligands similarly bearing S,S-donors tetraalkylthiuramdisulphides (Et_4TDS) in $(\text{CH}_3)_2\text{CO}$ have been used to quantitatively dissolve elemental gold under mild conditions producing gold-dithiocarbamate complexes [19].

Here, we present a process where the crucial step for gold recovery from real shredded selected PCB and other small electronic equipment, is based on the lixiviant properties of mixtures of the above cited reagents [dihalogen/S,S-ligands: N,N'-dimethyl-perhydrodiazepine-2,3-dithione (Me_2dazdt) or Et_4TDS in the presence of diiodine] in organic solvent. The recovery of copper and silver is also described to provide a whole process of satisfactory sustainability.

2 Materials and methods

Reagents and solvents were purchased from Sigma-Aldrich Chemie, Schenellndorf, Germany, and used without further purification.

2.1 Sample

The real sample is used as provided by a company which treats WEEE by applying a conventional mechanical process and consists of a milled mixture of metals which represent the non-ferrous metallic fraction output of the de-processing plant.

In this plant the raw material consists of PCBs and selected small electronic equipment, e.g., mobile phones, and this is submitted to crushing, separation from residual hazardous components, shredding and mechanical separation (magnetic and eddy current separation) of ferrous and non-ferrous metals and separation of the plastic.

2.2 Analytical characterization of the real samples

Samples of 0.5 g each were introduced in TFM (copolymer of PTFE, Polymer of TetraFluoroEthylene, with about 0.1% of PPVE, PerfluoroPropylene-VinylEther) vessels containing a mixture of HNO_3 (65%, 2 ml), HCl (37%, 6 ml), H_2O_2 (30%, 0.5 ml) and thus treated in a Milestone (Soriso, Bergamo, Italy) Ethos 1 Microwave digester, equipped with a HPR1000/10S high pressure segmented rotor, ATC-400CE automatic temperature control and Terminal 640 with easyCONTROL software. The treatment was performed applying a microwave program consisting of two steps lasting 10 and 20 min, respectively, at a temperature of 200°C and microwave power up to 1000 W. The samples were prepared for analysis by diluting the digested solutions with 1% HCl/HNO_3 blank and then the metals determined using a ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy) Varian (Palo Alto, USA) Liberty 200 Spectrometer, with respect to 5 point calibration plots in the 1–50 ppm range for copper and in the 1–10 ppm range for the other metals. Three independent experiments were used to determine the averaged values, which are reported in Table 1.

3 Results and discussion

3.1 Description of representative samples of WEEE

The samples which were submitted to the lixiviant process were the output of a mechanical de-processing plant, where a selection of PCBs and small electronic equipment were shredded and submitted to pretreatments in

Table 1 Metal content of the specimen sample.^a

Cu	79%
Sn	10%
Pb	7%
Zn	2%
Ni	0.5%
Ag	0.06%
Au	0.01%
Others (Al, Cr, Mn, Fe, Co)	1%

^aAverage composition on three independent determinations.

order to separate the incoming mixture into homogeneous particle flows, with high concentrations of target materials: aluminum, ferrous metals, vitreous-plastic materials and non-ferrous metals. Table 1 summarizes the metals content of the samples, which was determined by ICP-AES spectrometry, as described in the materials and methods section.

3.2 Process for the selective dissolution of metals from WEEE specimen sample

The process can be described in a sequence of three main steps, which allow selective removal of the lower noble metals, leaving as residue WEEE enriched in gold, the noblest and more valuable metal. Accordingly, the selected specimen milled sample was submitted to the following steps:

Scheme 1 Schematic representation of the “three-step” process, when the gold lixiviant is N,N′-dimethyl-perhydrodiazepine-2,3-dithione (Me₂dazdt)·2I₂.

LEACH 1. Treatment with refluxing HCl (1:5) under Ar atmosphere. This step produces dissolution of non-NMs with reduction standard potential lower than zero, leaving a residue which is collected to be submitted to LEACH 2;

LEACH 2. The residue of LEACH 1 is treated with NH₃/(NH₄)₂SO₄ in the presence of H₂O₂. This treatment allows copper and silver to be dissolved and removed by the milled sample;

LEACH 3. The residue milled sample of LEACH 2 is submitted to the final etching procedure, using Me₂dazdt or Et₄TDS/I₂ acetone mixtures, which allow gold dissolution.

Each dissolution step was followed by a further treatment for: (1) metal recovery, in the case of Au, Cu and Ag; and (2) inertization, in the case of heavy metals.

This process was employed on a laboratory scale, starting from 10 g of the milled sample described in Table 1. Scheme 1 summarizes the different leaching steps and relatable products, when, as an example, Me₂dazdt·2I₂ is used in LEACH 3. As shown, LEACH 1 allows the removal of base metals from the solid sample, which may be recovered from the aqueous solution by common treatments with suitable precipitating reagents. It was observed that a more effective separation of non-noble/noble metals is achieved if air is removed from the chlorine-rich reaction mixture. For this reason, Ar is employed during this step. LEACH 2 involves the treatment of the residue milled sample with ammonia (30%, 30 ml), ammonium sulfate (30 g) and gradual addition of hydrogen peroxide

(28%, 80 ml) until dissolution of metal copper and silver is achieved. The complete dissolution is checked by repeating the procedure on the solid residue until no change on the solution color occurs.

The solutions are collected and the metals recovered by electrowinning and/or chemical reduction. Finally, in LEACH 3, the solid residue is treated with an acetone solution of $\text{Me}_2\text{dazdt} \cdot 2\text{I}_2$ in a mass ratio 7:1 (lixiviant to metal). The gold dissolution produces a gold(III) complex (**1**) which has been fully characterized (see Scheme 2A). This complex reacts with Mg in the acetone solution producing elemental gold, MgI_2 and giving back Me_2dazdt .

For LEACH 3, as alternative etching reagent, acetone $\text{Et}_4\text{TDS}/\text{I}_2$ mixtures can be employed. Effective gold oxidation in mild conditions is achieved, and a gold(III) complex (**2**) (Scheme 2B) is obtained. In that case, the recovery of elemental gold and ligand are less straightforward and experiments are in progress to optimize the reaction.

3.3 Details on the gold leaching reaction

In this section, a summary of the reactions involving elemental gold and the etching reagents used in the process described above is provided for further information. Accordingly, the reaction conditions for the gold leaching by applying acetone solutions of Me_2dazdt or Et_4TDS in the presence of diiodine towards gold powder are reported in Scheme 2A and B, respectively.

It should be noted that S-donors are capable of interacting with diiodine to form donor-acceptor adducts in solution, as occurs in the cases under discussion [8, 20–22]. These adducts can also be stable in the solid

state, as observed for Me_2dazdt [9], or undergo further transformation for long standing in solution [21, 22]. Accordingly, in the $\text{Me}_2\text{dazdt}/\text{I}_2$ case the acetone solution can be prepared either by mixing the two components, or dissolving the adduct, whilst in the $\text{Et}_4\text{TDS}/\text{I}_2$ case, the etching solution is prepared by mixing the two components, since the adduct formation was observed in solution only and no neutral adduct was isolated in the solid state.

As summarized in Scheme 2, both lixivants are very effective towards gold powder and react readily through one-step reactions, which occur under mild experimental conditions producing **1** and **2** complexes. We note that these remarkable properties may be ascribed to an enhanced reactivity of the reagents due to the adduct formation. Further studies are required to better support this claim.

If the properties of the two gold-etching mixtures are compared, we observe that both reagents have fully satisfactory effectiveness in quantitatively recovering gold from e-waste in mild reaction conditions, both reagents are easy to handle, not toxic and do not produce toxic fumes. Moreover, both S-donors are available as solids which are easy to be stored and handled. These common features make both appealing for practical use. The easy availability, coupled with the low-cost of Et_4TDS , should make this reagent (which is already available on the market because it is widely used as a fungicide, for the rubber vulcanization process and as an anti-alcohol drug – disulfiram or antabuse) more appealing with respect to Me_2dazdt , which currently is not commercially available.

If the whole process to obtain elemental gold is taken into account, it may be remarked that chemical reduction of **1**, allows recovery of quantitatively elemental gold and Me_2dazdt in 60–100% yields, with a consequent cut of the costs and ligand consumption. Instead, the corresponding chemical reduction of **2**, does not allow ligand recovery. Nevertheless, the final product **2** has a high intrinsic value, since it could be employed as a precursor of valuable gold nanoparticles for application in catalysis [23].

The etching properties towards gold of reagents based on S-donors/diiodine mixtures in organic solvents seem to be suitable for practical applications; we wish to underline the fact that that in the proposed process, environmentally friendly and safe reagents to dissolve the different metals were used as much as possible. In particular, we avoided the use of toxic reagents or strong acid in high concentrations, particularly those which produce toxic fumes such as concentrated H_2SO_4 or HNO_3 , commonly used for copper and base metals leaching [2–4].

Scheme 2 Reaction schemes for gold leaching in acetone solution, by (A) the *N,N'*-dimethyl-perhydrodiazepine-2,3-dithione (Me_2dazdt) and (B) the tetraalkylthiuramdisulphide (Et_4TDS)/ I_2 mixtures.

¹ In the case of reaction (A), the diiodine $\text{Me}_2\text{dazdt} \cdot 2\text{I}_2$ adduct can be used in place of the mixture of the two reagents. $i=1:1.5:1$ molar ratio, room temperature, few min to dissolve 10 mg of gold powder; $ii=0.5:8:1$ molar ratio, room temperature, few min to dissolve 10 mg of gold powder.

4 Conclusions

We described a novel process based on a new approach for NMs recovery which appears to be a greener alternative to the conventional hydrometallurgy treatments commonly in use. This method allows the recovery of gold, silver and copper from WEEE, which is a difficult material to be treated due to the intrinsic complexity of its composition. Reported here are examples of remarkable Au etching capability exhibited by donor–acceptor mixtures in organic solvents. A suitable mixture formulation for these novel etching reagents may be predictable, depending on which application is required. Given the wide range of applications, ranging from the recovery/recycling

of scrap materials to failure analysis of microelectronic devices, the most suitable formulation should be tailored depending on which aspect is important (i.e., efficiency, homogeneity, rate, cost, recyclability, nature of reagents, product value, metal recovery, etc.).

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