



# **Valorization of Mining Waste by Application of Innovative Thiosulphate Leaching for Gold Recovery**

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Received: 18 January 2019; Accepted: 23 February 2019; Published: 28 February 2019



**Abstract:** The metals and industrial minerals contained in the tailings of mining and quarrying activities, can degrade natural environments as well as human health. The objective of this experimental work is the application of innovative and sustainable technologies for the treatment and exploitation of mining tailings from Romania. Within this approach, the recovery of high grade raw materials to be placed on the market is achieved and reduction of these wastes volume are achieved. The current study is focused on hydrometallurgical process for the recovery of gold. The innovative treatment chosen is the thiosulphate process that, compared with the conventional cyanide, has several advantages (e.g., it is more ecologically friendly and is not toxic to humans). The conventional cyanidation process shows operating limits in the case of auriferous refractory minerals, such as Romanian wastes, the object of the study. An important characteristic of thiosulphate leaching process it has the best selectivity towards gold; it does not attack the majority of the gangue mineral constituents. Gold extraction of 75% was obtained under ambient conditions of temperature. Moreover, the overall process achieved about 65–67% Au recovery, this being in line with the conventional cyanidation process. As these results are obtained by application of the thiosulfate process on a low gold content ore, they may be considered encouraging. The optimization of process parameters and operating conditions, should permit the best results in terms of process yields to be achieved.

**Keywords:** mining waste; hydrometallurgical processes; leaching kinetic; thiosulphate leaching; electrowinning; gold

# **1. Introduction**

Several studies have shown that mining activities can significantly damage, pollute and alter the environment (e.g., soil, sediments, water and air quality) as well as human health [\[1–](#page-10-0)[4\]](#page-10-1). Furthermore, mining involves the creation of surface features that are unstable, prone to landslides and collapses, but, especially, expose the environment to exogenous vast areas of mineralized rocks and byproducts of mineral treatment. These outcomes produce significant changes in the chemical environment [\[5,](#page-10-2)[6\]](#page-10-3). The large volumes of wastes produced by mining occupy huge areas; these accumulations can substantially change the original landscape.

Alongside mining, mining wastes, if managed properly, can be important to the economic growth of countries. The application of a proper treatment ensures environmental sustainability and minimize



the risks to human health. In fact, the deposits of mining tailings should not be treated as inert wastes, but as a neo-mine: only a short-sighted vision would be limited solely to neutralize the harmful and toxic waste stored and to put in place procedures and interventions that allow the restoration of the original environmental conditions.

Instead, the enhancement of the tailings, in addition to the sale of raw materials grade high (precious metals such as gold), allows a complete and effective recovery of environmental conditions sustainable because the recycling activity also determines an economic convenience for the treatment.

Romania, like many other nations affected by a long history of mining, is now grappling with environmental and social issues related to tailings produced by mining activities. On the Romanian territory a total of 300 tailings deposits, produced by exploitation of different minerals, have been inventoried. All are of significant proportion and should be submitted to amelioration procedures, such as the neutralization of treatment residues [\[7](#page-10-4)[,8\]](#page-10-5). These waste materials are a result of mining activities that have reached the end of the production cycle due to depletion of the reservoir or, after stopping of the process for environmental reasons (i.e., regulations put in place at the time of the Convention for Romania's entry into the EU). In Romania, the administration of these landfills is carried out by the Romanian National Agency for Mineral Resources (ANMR). The mining sites considered within this study are Bălan, Deva deposit 1, Deva deposit 2, Brad Ribita and Brad Criscior. Mine Bălan, for example, which ceased its operations in 2006, under the Convention for the entry of Romania into the EU, is a tabular deposit tectonized in metamorphic rocks. The main mineral is chalcopyrite. The remaining reserves amounted to 500,000 tonnes at 0.8% of copper content. These reserves are substantially unavailable. The costs of re-mining and carrying out of modifications to enrich the mineral are too high compared to the value of resources and costs of extraction [\[7–](#page-10-4)[10\]](#page-10-6).

The deposits of tailings, left on the land during the mining of copper ore, contain 24.5 million tonnes of slag and more than 10 million cubic meters of materials that constitute a toxic and harmful waste. These deposits are located at a distance of few kilometers from the mining center (at the neighborhood of the Bălan town) [\[7](#page-10-4)[,8\]](#page-10-5).

The removable high-grade raw materials, from the tailings of Bălan, like those of the other mentioned sites, are:

- industrial minerals, such as quartz, pyrite and chlorite, recoverable through metallurgical processes;
- base metals, including copper and zinc, and precious metals such as gold and silver, extracted with hydrometallurgical processes.

The aim of this work is to apply innovative technologies for the treatment and exploitation of Romanian mining tailings. In particular, this study is focused on the development of an hydrometallurgical process for the recovery of gold from solid wastes of mining industry. The innovative treatment chosen was the thiosulphate process, that has advantages over the conventional cyanide and is non-toxic to humans; in fact, it is environmental impact is lower than for cyanidation [\[11](#page-10-7)[–18\]](#page-11-0).

The kinetics of the thiosulphate process has been studied with the main aim to improve the characteristics that distinguishes from the conventional cyanide process for gold recovery. The main potential advantages of this innovative treatment for gold recovery, can be summarized in the following points:

- 1. solubilization of gold with an appreciable rate of dissolution;
- 2. ammonia-containing solutions do not attack most of the gangue mineral constituents;
- 3. production of leach solutions, practically free of metallic elements that hinder the subsequent recovery operations;
- 4. ability to recirculate the ammonia leaching solutions;
- 5. non-toxicity of the reagents used in the leaching process;

6. possibility for recovery of the dissolved gold by known techniques, such as carbon adsorption and electrodeposition.

The greatest criticality of the process is constituted by the chemistry of the ammonia-thiosulphate system, that is very complicated due to the simultaneous presence of complexing ligands such system, as ammonia and thiosulphate, the Cu(II)–Cu(I) redox couple and the possibility of oxidative decomposition reactions of thiosulphate involving the formation of additional sulphur compounds  $\alpha$ such as tetrathionate [\[11\]](#page-10-7). and  $\alpha$  and  $\alpha$  is very complicated due to the system, that is very complicated due to the simulation of suitabling possibility of oxidative decomposition reaction reaction reaction reaction of the formation of the formation of

The ultimate purpose of this work is to develop a process scheme on the basis of results obtained  $\frac{1}{2}$ . at laboratory scale. This will be used to perform a preliminary study of the technical feasibility of at laboratory scale. This will be ased to perform a preliminary study of the technical reasionity of process. Figure [1](#page-2-0) shows an example of a mining site with tailings from Romania. feasibility of process. Figure 1 shows an example of a mining site with tailings from Romania.

<span id="page-2-0"></span>

**Figure 1.** Tailings of a mining site in Romania. **Figure 1.** Tailings of a mining site in Romania.

# <span id="page-2-1"></span>**2. Materials and Methods 2. Materials and Methods**

# **Sampling**  *2.1. Sampling*

The mining sites under study were: Bălan, Deva deposit 1, Deva deposit 2, Brad Ribita and Brad The mining sites under study were: Bălan, Deva deposit 1, Deva deposit 2, Brad Ribita and Brad Criscior. For each mining site homogeneous and representative samples were prepared for Criscior. For each mining site homogeneous and representative samples were prepared for subsequent enselof. To the final and site homogeneous and representative samples were prepared to subsequent characterization. To this end, after being dried in oven at 80 °C for one day and sieved to 4 mm, the 4 mm, the fractions were then homogeneously and representatively sampled using a RETSCH rotary fractions were then homogeneously and representatively sampled using a RETSCH rotary splitter. splitter. From each site, eight samples were collected. From each site, eight samples were collected.

For the characterization of the particles sizes, the prepared samples were quartered with a For the characterization of the particles sizes, the prepared samples were quartered with a manual manual samples to the submitted to we submit the submitted to we shall be a strong size. sampler and submitted to wet sieving using sieves of following sizes: 0.5 mm, 0.351mm, 0.250 mm,<br>19425 - The children of the ch over a 80 mm. The bounded grandformed the basis were intered, dried in a hoordrofy overfactor  $\epsilon$ for one day and then weighed. On the basis of the obtained weights, the distribution curves were and 0.125 mm. The obtained granulometric fractions were filtered, dried in a laboratory oven at 80 ◦C constructed (data not showed here).

For each mineral deposit, one of the eight prepared samples was submitted to gravimetric For each mineral deposit, one of the eight prepared samples was submitted to gravimetric separation by a flow table. The flow table. The four fractions of the flow table. The flow of the flow separation by a flow table. The four fractions obtained (light, intermediate, mixed and heavy) were<br>Site of the little in the consideration and the consideration of the consideration of the consideration of the  $T_{\rm eff}$  rotation of separation of sample into various fraction of sample into various  $\omega$ filtered, dried in a stove at 80  $\mathrm{^{\circ}C}$  for a day and then weighed.

This rotary splitter allows the separation of sample into various fractions whose composition  $\frac{1}{2}$ corresponds exactly to that of the initial sample, because only a representative sample of the initial rate This procedure ensures a high degree of accuracy and reproducibility. It is used in combination can provide significant analytical results.

This procedure ensures a high degree of accuracy and reproducibility. It is used in combination<br> $T_{\text{eff}}$ with the vibrating feeder RETSCH DR 100, utilized for the homogeneous and uniform assay during<br>with the vibrating feeder RETSCH DR 100, utilized for the homogeneous and uniform assay during the conveying of the material; this is an automatic process of sampling, without interruptions and loss  $\frac{1}{2}$  planetary ball mill mill agate model mill agate model for the fine grinding of the fi of material. The speed was monitored and kept constant.

A planetary ball mill agate mod. FRITSCH pulverisette, was used for the fine grinding of the samples. The jars and grinding balls were made of agate to prevent samples contamination.

#### *2.2. Characterization*

The mineralogical characterization was carried out by the technique of X-ray diffraction (X-ray diffractometer Bruker, mod. D8 Advance).

The analytical determination of metals and gold content of the fractions obtained from the table, was carried out by Perkin Elmer, mod. 400 optical plasma spectrometer (ICP-AES) with data station. This analysis was performed on the solutions achieved after sample chemical dissolution.

Homogeneous and representative samples of approximately 10 g, submitted to chemical attack, were prepared by rotary and manual splitters and subsequently milled in a planetary mill with agate jars and balls. The milling was performed till the particles sizes was less than 80  $\mu$ m, this being appropriate for the subsequent leaching tests [\[11\]](#page-10-7). The sample for gold recovery tests was chosen considering the gold content.

The experimental work was carried out on the heavy fraction constituted by a mix between Brad Ribita and Brad Criscior samples, which had an average gold content of  $3 g/t$ .

#### *2.3. Physical Process*

The samples from mining sites Brad Ribita and Brad Criscior, chosen for their higher gold content, were sieved to −0.5 mm, and the fractions submitted to gravimetric separation by the flow table. The table was set with the aim to obtain a richer heavy fraction The heavy fractions recovered were filtered and dried in a stove at 80  $\mathrm{^{\circ}C}$  for one day.

#### *2.4. Grinding*

The heavy fractions, obtained by gravimetric separation, were subjected to comminution  $\left( \langle 80 \rangle \mu \text{m} \right)$ , using a bar mill, to make them suitable to determination of the content of gold and for the subsequent leaching tests. The grain sizes obtained were analyzed with the SYMPATEC laser granulometer.

At the end of the comminution, the drum was emptied and the slurry after being filtered was dried in a stove at 80  $\degree$ C. The heavy fractions, after comminution, were mixed homogeneously using the rotary splitter to prepare samples of the mix Brad Ribita-Brad Criscior, and submitted to leaching tests. The gold content of the mixture of minerals was determined after chemical dissolution, with an Atomic Absorption Spectrometer (AAS Perkin Elmer mod. 460).

## *2.5. Chemical Process*

The study of the thiosulphate process, was conducted in mechanical stirred reactors made of Pyrex glass that have a capacity of 2000 mL. Leaching experiments were carried out to study the influence of the concentration of ammonia and the concentration of thiosulphate on gold dissolution, using reagents of analytical grade and distilled water.

The leaching solutions consist of sodium thiosulfate  $(Na_2S_2O_3·5H_2O)$ , used as active leaching agent, ammonia ( $NH_4OH$  30%)—for the control of pH—and copper (II) sulphate  $(CuSO<sub>4</sub>·5H<sub>2</sub>O)$ —which acts as an oxidant of gold [\[11](#page-10-7)[,16](#page-11-1)[,17\]](#page-11-2).

The tests were carried out at atmospheric pressure and room temperature, while the speed of mechanical agitation was kept constant at 400 rev/min. The leaching time was 4 h, the weight of the samples of 500 g, the particle size minus 80  $\mu$ m, pH of 10.5 and a redox potential +0.1 V. At set time intervals, small volumes (10 mL) of leaching solution were taken from the reactor. These were analyzed to determine their Au content and, therefore for the kinetic study of gold dissolution [\[19](#page-11-3)[,20\]](#page-11-4).

The pH and the oxidation-reduction potential of the slurry, were measured using a combined glass electrode and a platinum combination electrode, respectively, both being connected to a digital pH meter.

At the end of each test, the reactor was emptied, while the filtration of the slurry was realized through pressure filters. The solid residue was submitted to washing with distilled water and ammonia; moreover, gold content was determined, after chemical dissolution of homogeneous and representative samples, with an Atomic Absorption Spectrometer (AAS Perkin Elmer mod. 460).

After leaching, the gold was purified by selective adsorption onto granular activated coconut carbon. The influence of the carbon concentration was studied.

This was conducted in Pyrex glass reactors of capacity of 2000 mL under mechanical stirring (400 rev/min), at room temperature, for a total contact time of 1 hour [\[20–](#page-11-4)[22\]](#page-11-5).

The tests were carried out by placing in contact leached solution (500 mL) with the different amounts of coconut charcoal, an activated carbon material. The influence of the contact time was investigated by performing liquor withdrawals at set intervals. The concentration of the activated carbon was varied from  $5 g/L$  to  $15 g/L$ . After each experiment, carbon was recovered from the solution and left air drying. Representative samples of carbon were collected and submitted to quantitative chemical analysis.

The desorption of gold from carbon was carried out by elution with a water-ethyl alcohol solution prepared using absolute ethanol ( $C_2H_5OH$ ) [\[22\]](#page-11-5). The gold stripping tests were conducted in a Pyrex glass reactor, with a capacity of 250 mL. The reactor was fitted with three necks: the first one had reflux condenser for the removal of vapors, the second one housed a probe that was connected to a shaking-heating plate for stabilizing the temperature and a thermometer for temperature control was inserted through the third port. The tests were conducted varying the temperature from 40 to 85  $°C$ .

Sampling was performed also at determined time intervals and then chemically analyzed to determine their Au content. These data were used to determine the kinetics of the process.

The final recovery of purified metallic gold from the water-alcohol solution, was carried out by the electrochemical process [\[19,](#page-11-3)[20,](#page-11-4)[23\]](#page-11-6).

Gold recovery conducted in an electrolytic cell with a capacity of 200 ml in a jacketed Pyrex glass, connected to a Julabo, mod. 5B thermostat (control from −20 to +100 ◦C). The cell was fitted with a saturated calomel reference electrode, a working electrode (cathode) constituted by a net of platinum wire, having a surface area of 100 cm<sup>2</sup>, and a counter-electrode (anode) consisting of a spiral platinum.

The cell was connected to a AMEL, model 555 B potentiostat-galvanostat. The current flowing through the cell was converted into a numerical value by an AMEL, model 721 integrator. The potential difference between the cathode and the anode was measured with an AMEL, model 631 differential electrometer.

The presence of a magnetic stirrer bar allows stirring of the solution into the cell. The electrolysis tests were conducted using 200 mL of strip solution.

## **3. Results**

#### *3.1. Physical Process*

The homogeneous and representative samples, achieved after screening, to retain particles with a diameter greater than 0.5 mm, were submitted to gravimetric separation by the flow table. The goal of the physical process was to concentrate pyrite, and then the gold associated with it, in the heavy fraction. The light fraction consists predominantly of quartz.

The heavy fraction for none of the deposits reaches 10%, therefore we must consider that most of the pyrite could be concentrated in the mixed fraction. For all sites the light fraction exceeds 40%, with over 61% in Balan samples.

The chemical analysis, allowed the gold content of the mixed fractions and heavy minerals to be studied. Based on this data the mining sites of greatest interest from the point of view of the gold content are: Brad Ribita and Brad Criscior. These sites were chosen to the study the process of Au recovery. The X-ray diffraction performed on the heavy and mixed fractions from Brad Ribita and Brad Criscior allowed the mineralogical composition to be determined. In detail, the mineralogical species contained in the heavy fraction Brad Ribita are the following: quartz— $(SiO<sub>2</sub>)$  (48.3%); pyrite (FeS<sub>2</sub>) (20.4%); muscovite—(K, Ba, Na)<sub>0.75</sub>(Al, Mg, Cr, V)<sub>2</sub>(Si, Al, V)<sub>4</sub>O<sub>10</sub>(OH, O)<sub>2</sub> (15.5%);

albite—(Na<sub>0.75</sub>Ca<sub>0.25</sub>)(Al<sub>1.26</sub>Si<sub>2.74</sub>O<sub>8</sub>) (8.7%); chamosite—(Mg<sub>5.036</sub>Fe<sub>4.964</sub>)Al<sub>2.724</sub>(Si<sub>5.70</sub>Al<sub>2.30</sub>O<sub>20</sub>)(OH)<sub>16</sub>  $(4.9\%)$ ; Calcite—CaCO<sub>3</sub> (2.1%) and Chalcopyrite—CuFeS<sub>2</sub> (0.1%).

The following main elements have been determined by chemical analysis of the heavy fraction Brad Ribita: Si (27.0%), S (11.0%), Fe (10.6%), Al (3.3%), V (3.1%), Ca (1.2%), Ba (1.2%), Mg (0.9%), **Ma** (0.8%).

Regarding heavy Brad Criscior, the mineralogical composition is constituted by:  $quartz-(SiO<sub>2</sub>)$ (66.2%); pyrite (FeS<sub>2</sub>) (10.2%); muscovite—(K, Ba, Na)<sub>0.75</sub>(Al, Mg, Cr, V)<sub>2</sub>(Si, Al, V)<sub>4</sub>O<sub>10</sub>(OH, O)<sub>2</sub> (14.2%); albite—(Na<sub>0.75</sub>Ca<sub>0.25</sub>)(Al<sub>1.26</sub>Si<sub>2.74</sub>O<sub>8</sub>) (5.1%); chamosite—(Mg<sub>5.036</sub>Fe<sub>4.964</sub>)Al<sub>2.724</sub>(Si<sub>5.70</sub>Al  $_{2.30}O_{20})$ (OH)<sub>16</sub> (2.9%); Calcite—CaCO<sub>3</sub> (1.1%) and Chalcopyrite—CuFeS<sub>2</sub> (0.3%).

Main elements detected by chemical analysis of the heavy fraction Brad Criscior are: Si (33.9%), S (5.5%), Fe (5.4%), V (2.9%), Al (2.5%), Ba (1.1%), Cr (0.8%), Ca (0.6%), Mg (0.7%), Na (0.5%), K (0.3%),  $Cu (0.1\%).$ 

FeS<sub>2</sub> in the mixed fraction for Brad Ribita is 6.3%.

<span id="page-5-0"></span>The results of the gravimetric separation are shown in the following Table [1.](#page-5-0)

Fraction	$\frac{1}{2}$
Heavy Brad Ribita	8.0
Heavy Brad Criscior	12.0

**Table 1.** Heavy fractions separated from the flow table.

## **3.2. Chemical Process**

# 3.2.1. Gold Leaching

The experimental work was carried out on the heavy fraction, mix of the Brad Criscior and Brad Ribita samples, with an average gold content of 3 g/t. Gold was recovered by leaching with sodium thiosulphate as previously described. The gold content with with the washing solution and solid residue of the washing solution and solution and

After the preliminary experiment—carried out using conditions from the literature [\[11](#page-10-7)[,15\]](#page-11-7) leaching enabled a gold recovery of 38.10% (for the calculation of efficiency there was considered also the gold content within the washing solution and solid residue). The investigation permits the influence and the interactions between S<sub>2</sub>O<sub>3</sub><sup>2−</sup>, CuSO<sub>4</sub> and NH<sub>3</sub> concentration on gold kinetics to be studied (Figures 2 and [3\)](#page-6-0).

<span id="page-5-1"></span>

**Figure 2.** The influence of  $NH_3$  concentration on gold recovery (2 M  $Na_2S_2O_3$ ; 0.1 M  $CuSO_4$ ).

<span id="page-6-0"></span>

**Figure 3.** The influence of  $S_2O_3^{2-}$  concentration on gold recovery (4 M NH<sub>3</sub>; 0.1 M CuSO<sub>4</sub>).

influence of  $S_2O_3^{2-}$  concentration. In both cases, CuSO<sub>4</sub> concentration was constant at 0.1 M [\[11](#page-10-7)[,14](#page-10-8)[,22\]](#page-11-5): the thermodynamic condition that allows the best gold recovery was achieved with a solution of the following composition: 2 M S<sub>2</sub>O<sub>3</sub><sup>2−</sup>, 0.1 M CuSO<sub>4</sub> and 4 M NH<sub>3</sub>. Figure [2](#page-5-1) shows the influence of NH<sub>[3](#page-6-0)</sub> concentration on gold recovery, while Figure 3 shows the

washing). It was observed that the kinetics of extraction decreases by approximately 20% at the end of the experiment (about 65% Au after 4 h, with washing) [\[11\]](#page-10-7). Table [2](#page-6-1) describes the best kinetic with higher gold recoveries (about 75% Au after 15 min, without

Time (h)	$Au$ (mg)	Au Recovery (%)
0.25	0.91	73.38
0.5	0.90	72.31
1	0.86	69.63
1.5	0.82	66.95
$\overline{2}$	0.74	60.52
3	0.73	59.99
4	0.74	60.52
Washing	0.033	2.33

<span id="page-6-1"></span>**Table 2.** Gold recovery obtained with a ammoniacal leaching solution having the following composition:  $2 \text{ M } \text{S}_2\text{O}_3{}^{2-}$ , 0.1 M CuSO<sub>4</sub> and 4 M NH<sub>3</sub>.

The following Table [3](#page-6-2) shows the parameters that allowed the best gold leaching kinetics.

<span id="page-6-2"></span>

Parameters	<b>Values</b>
Temperature $(^{\circ}C)$	25
Particle size (µm)	< 80
Pulp density ( $w/v$ %)	50
pH	10.5
Stirring conditions (rpm)	400
Time of treatment (h)	<1
$S_2O_3^{2-}$	2 M
CuSO <sub>4</sub>	0.1 <sub>M</sub>
NH <sub>3</sub>	4 M

**Table 3.** Best process parameters of the gold leaching.

The goals of the further work will be to optimize the leaching process conditions, with the aim to increase gold extraction yields, and to reduce the reagents consumption, such as the concentration of thiosulphate used.

#### 3.2.2. Gold Adsorption

The leaching solution containing gold in the form of soluble complex, is placed in contact with the activated carbon to selectively separate the gold by adsorption. The experimental conditions described in Section [2,](#page-2-1) were applied to study the influence of the mass ratio of carbon to solution on the gold recovery process. The purification process of the solutions achieved after leaching allowed high gold recoveries to be obtained (Table [4\)](#page-7-0).

<span id="page-7-0"></span>

Time (min)	5 g/L Carbon % Au	10 g/L Carbon % Au 15 g/L Carbon % Au	
15	53.59	50.00	82.05
30	61.54	70.52	98.72
45	76.65	87.18	98.72
60	85.90	98.72	98.72

**Table 4.** Kinetics of Au adsorption at different concentrations of carbon in solution.

The results show an almost complete recovery of the gold present in solution. From the trend it is clear that the increase of the concentration of carbon in solution favors the recovery. In particular, after 1 h, at a concentration of carbon of  $5 g/L$ , about 86% Au was adsorbed, but the recoveries reach 99% Au when the concentration of the adsorbent increases to  $10 g/L$ . Also it was found with a concentration of 15 g/L, that 99% Au adsorption was achieved after only 30 min.

<span id="page-7-1"></span>The parameters that allowed the best gold adsorption onto activated carbon have been reported in Table [5.](#page-7-1)

Parameters	Value
Temperature $(^{\circ}C)$	25
Carbon concentration $(g/L)$	15
рH	10.5
Stirring conditions (rpm)	400
Time of treatment (min)	חר

**Table 5.** Best process parameters of gold adsorption on activated carbon.

### 3.2.3. Gold Desorption

The purpose of desorption was to re-extract the gold adsorbed and concentrate it. The duration of process was fixed at 6 h.

<span id="page-7-2"></span>From the experimental results, shown in Table [6,](#page-7-2) it can be observed that the final gold recovery was of 79.0%: further studies using other types of alcohol such as isopropyl alcohol and ethylene glycol, may improve the efficiency, shortening the duration of the stripping process.

**Table 6.** Kinetics of Au desorption at different concentrations of carbon in solution.

Time (h)	$Au$ (mg)	Au Yield (%)
1	0.20	18.0
$\mathcal{L}$	0.34	30.0
4	0.46	41.0
6	0.88	79.0
Washing	0.30	20.0

<span id="page-8-0"></span>The process parameters for the desorption of gold from activated carbon that permitted to achieve 99.0% Au recovery—including washing—after 6 h, are shown in Table [7.](#page-8-0)

<b>Parameters</b>	Value	
Temperature	$80^{\circ}$ C	
Speed of agitation	300 rpm	
Time of extraction	6 h	
Mass ratio of coal and stripping solution	75 g/L	

**Table 7.** Best process parameters of gold desorption from the activated carbon.

#### 3.2.4. Electrowinning

The last step of the process was electrowinning. The goal of this step was the recovery of gold from the strip solution by cathodic deposition of the metal. Table [8](#page-8-1) shows the experimental results obtained. Table [9](#page-8-2) shows the optimized process parameters of the phase of gold electrodeposition.

**Table 8.** Experimental gold electrowinning parameters.

<span id="page-8-2"></span><span id="page-8-1"></span>

Time (min)	Cathodic Voltage (V)	Cell Voltage (V)	Current Intensity (mA)	Electric Charge (C)
15	1.4	2.25	100	161
30	1.4	2.51	210	254
45	1.4	2.47	210	352
60	1.4	2.52	210	448
75	1.4	2.51	210	564

**Table 9.** Best process parameters of the phase of gold electrodeposition.



The kinetics of electrodeposition in cell of laboratory is quick and the final metallic gold recovery was high (98% Au). The concentration of gold in the sterile solution was below the detection limit of the instrument) after the first 30 min. A dark deposit was uniformly distributed on the surface of the cathode.

From the reported data, it was noted that the intensity of the measured current is around 210 mA, which corresponds to a current density of about 2.1 mA/cm<sup>2</sup>, given that the cathode surface is 100 cm<sup>2</sup>. As can be seen from the experimental results, the amount of charge that passes through the cell after 30 min was 254 Coulombs. Hence the current efficiency was low (5%); this is due to parasitic reactions, such as the reduction of the water and of dissolved oxygen. The consumption of energy was high; about 20 kWh/kg of gold deposited.

# **4. Discussion**

The preliminary study of the parameters and operating conditions for the various stages of the thiosulphate process shows, for the sample composed of mining wastes from Brad Ribita and Brad Criscior, the technical viability of the process. The experimental results obtained indicate good gold dissolution kinetics in the aqueous ammoniacal solution of thiosulphate, which can be used without special precautions and restrictions.

The gold extraction reached an average final value of 75% Au, working at room temperature, but, the trends for dissolution demonstrate that the thermodynamic parameters were not optimized, because gold recovery decreases during the best experiment. This fact, probably, is due to the thermodynamic instability of the complexing ligands (ammonia and thiosulphate) and oxidizing agents (copper ions) present in the system, tested for the first time on this type of material [\[11](#page-10-7)[,24\]](#page-11-8).

It is noted that the extraction of gold is already very high in the first 15 minutes: this is due to the gravimetric enrichment and means that a part of the gold is free and is not incorporated into the mineral matrix (see Table [2\)](#page-6-1).

Gold recoveries for the overall process including leaching (extraction yield of about 75% Au) and complete adsorption-desorption–electrodeposition cycle (about 90% Au recovered) were about 65–67% (considering the gold content in the washing) in line with the conventional cyanidation process, as demonstrated in previous experimental work [\[25\]](#page-11-9).

These results are very encouraging, considering that it is commercially an innovative process, applied to a gold ore with a low content.

Samples were leached after comminution  $<80 \mu m$ : a finer grinding would probably result in an increase in gold extraction, but its convenience can only be determined after careful cost analysis.

The optimization of the process is still required to identify the best process parameters and operating conditions. Considering the progressive depletion of gold mining reserves and the inability of the gold production to quickly react to the prospect of a change in prices and to changes in demand, it is providential to recover gold from mining tailings. The high price of the precious metal allows, as preliminary economic analysis shows, the feasibility of alternative processes despite the low levels of gold, the large amount of sterile to be treated and the high costs of extraction.

The enhancement of the tailings, in addition to the sale of raw materials of high grade, allows to implement an effective and sustainable recovery technology. In this way it is possible to guarantee over time the use of two indispensable resources of primary importance: the environment as a whole on one side and raw materials mining the other.

In addition to the economic and environmental aspects, we must consider the social benefits that the application of these innovative processes may generate such as providing many jobs and contributing thus to the development of repressed areas, improving the competitiveness of and creating added value and new jobs in raw materials processing, refining, equipment manufacturing and downstream industries.

In the next step of investigation, pre-treatment of components such as pyrite will be investigated before the extraction of gold. For this purpose a treatment circuit that employs biotechnological processes, with low energy consumption, will be integrated.

The elimination of pyrite will help to reduce the cost of extracting gold, reducing the consumption of the reagents. The application of physical-chemical and biological-chemical methods will allow the treatment of the Acid Mine Drainage, together with the recovery of heavy metals such as copper [\[26\]](#page-11-10); moreover, the optimization of leaching kinetics will be performed. The complete leaching process analysis will be outlined, including detailed description of the process scheme together with the economic analysis.

#### **5. Conclusions**

The present work examined a potential innovative application of a treatment for gold recovery, based on the thiosulphate process.

The challenge here was to apply it to the recovery from resources with low gold content. The preliminary application of this circuit allowed the following results in the various steps to be obtained:

- (1) Leaching: the gold extraction reached a final value of about 75% Au at room temperature.
- (2) Purification (adsorption/desorption on/by activated carbon and electrowinning) about 90% Au.
- (3) Recoveries of the overall process of about 65–67% Au, in line with the conventional cyanidation process.

These results are very encouraging, considering that this is a commercially innovative process, applied to a low gold content ore.

The next objective is to study parameters that allow the improvement of the gold dissolution kinetics and the subsequent steps of recovery from purified solutions, thereby determining beforehand the technical feasibility of the scheme of process developed at the laboratory scale.

The optimization of process parameters and operating conditions, and scale up of the process at industrial level will permit the best results in terms of process yields to be achieved, and in turn will allow us to exploit important resources for the European economy.

**Author Contributions:** Conceptualization, F.V. and V.G.; Data curation, F.V. and D.G.; Formal analysis, S.U. and F.V.; Investigation, D.G.; Methodology, D.G.; Supervision, S.U.; Writing—original draft, S.U.; Writing—review & editing, S.U. and V.G.

**Funding:** The work was supported financially by the Istituto di Geologia Ambientale e Geoingegneria, CNR, through special funds for free theme research.

**Acknowledgments:** This experimental work was carried out during the course of the experimental degree thesis of Dr. Alessia Panone from Università degli Studi dell'Aquila. The authors are grateful to Dr. Alessia Panone and Mr. Pietro Fornari for their helpful collaboration during the experimental work.

**Conflicts of Interest:** The authors declare no conflict of interest.

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