AN ENVIRONMENTALLY BENIGN APPROACH FOR GOLD RECOVERY FROM GOLD-BEARING ORE: MODELING AND OPTIMIZATION

Meschack Mukunga MUANDA[1,*], Pele Pascal Daniel OMALANGA[2], Anaïs Belembo ANNYFA[3], Vanessa Mwambaie MITONGA[4], Michée Ngoy ILUNGA[5]

[1]Chemical Engineering Department, Faculty of Engineering, Alexandria University, Alexandria, Egypt
[2]Department of Industrial Chemistry, Faculty of Polytechnic, University of Lubumbashi, Lubumbashi, Democratic Republic of the Congo
[3]Chemical Process Engineering Department, School of Industrial Engineers, University of Lubumbashi, Democratic Republic of the Congo
[4]Civil Engineering Department, School of Industrial Engineers, University of Lubumbashi, Democratic Republic of the Congo
[5]Electrical Engineering (Computer Engineering) Department, School of Industrial Engineers, University of Lubumbashi, Democratic Republic of the Congo

Abstract

The current work focuses on the extraction of gold using alpha-cyclodextrin (α-CD) from the Kimpese quarry in the Democratic Republic of the Congo, through an environmentally friendly gold process as an alternative to the amalgamation process. The ore was sampled and characterized using atomic absorption spectroscopy (AAS) prior to the experiments, and the analysis revealed 0.08% of gold. The ore was then leached with modified aqua regia (MAR). Time, HBr concentration, pH, and stirring speed were all varied during leaching to highlight the parameters that influence the leaching yield. The optimum conditions were determined using analysis of variance (ANOVA) and response surface methodology (RSM), implying time, HBr concentration, pH, and stirring speed of 6 hours, 80g/l, 1, and 800rpm, respectively, and a leaching percentage of 98.6928%. Following leaching, neutralization tests with potassium hydroxide (KOH) were performed by varying the following parameters: time, KOH concentration, and pH. The following factors were varied in the extraction tests after neutralization: time, α-CD concentration, pH. The optimal parameters were as follows: time of 30 minutes, α-CD concentration of 8.8639g/l, and pH of 6, with yield of 17.7350%. This method of recovering gold from ore using α-CD is inexpensive and does not harm the environment.

Keywords*: Alpha cyclodextrin, Extraction, Gold, Modeling, Modified aqua regia, Response surface methodology.*

Introduction

Gold was one of the first metals worked by man, and it has been used for decoration and jewelry since the middle ages. It is an exceptional metal due to its physio-chemical properties, which include being a good conductor, ductile, malleable, resistant to oxidation, and one of the least reactive metals. It is also significant in the economy, finance, and industry. Gold is found in low concentrations in the earth's crust, 0.004 mg per ton, which helps to explain its high market price [1]. It is found in its natural state as nuggets, which may have been mechanically eroded to powder or flakes. The vein, inclusion in ultrabasic rocks, and alluvial deposits resulting from fluvial erosion of the source rocks are the various forms of its distribution in its native state [2].

---

*Corresponding author: es-meschack.mukunga@alexu.edu.eg

There are two types of gold: primary gold, which comes from tectonic and volcanic activity and generally occurs in the form of veins or layers in the rocks, and secondary gold, which comes from the erosion of the primary gold-containing rocks over tens of millions of years due to exposure to tropical climatic conditions. Furthermore, secondary gold is found in alluvium, river terraces, and eluvium in the form of powder, flakes, or even nuggets [3]. It is also known that many minerals contain many metals in different proportions [4-5]. In nature, gold is frequently found in its native state and/or alloyed with other metals such as silver, copper, and cobalt. The most common oxidation state for it is zero (0) [6]. However, its relative chemical inertness protects it from dioxygen attacks, i.e. metallic gold does not tarnish or form oxide regardless of temperature, and it also resists the action of many chemicals, including most acids [7-9]. Gold can be dissolved by cyanide and aqua regia, which are made by combining three parts concentrated hydrogen chloride (HCl) and one part concentrated nitric acid (HNO_3) [10-12]. In medicine, gold is important in the treatment of joint problems such as rheumatism. Drugs based on metallic gold bathed in colloidal solution can also be used to treat rheumatoid arthritis and certain cancers. Although ceramics are becoming more popular in dentistry, gold is still widely used for fillings, crowns, and other orthodontic applications [13-14]. The ability to create various gold-based alloys adds to its effectiveness in the jewelry industry [15-16].

Gold is primarily used in electronics, where it is valued primarily for its electrical conductivity. Almost all electronic components contain a trace of gold: mobile phones, computers, GPS devices, and televisions [17-19].

Small amounts of gold are used in the production of special glasses, such as those used on modern building facades. The gold, whether dispersed within the glass panel or applied as plating, serves to reflect solar radiation, allowing the building to stay cool in the summer. In the winter, it helps to reflect internal heat inwards, allowing the building to retain heat [20-21].

In the metallurgical industry, gold cyanide (in solution) is used in thermostatically controlled and agitated electrolysis baths to control deposits in the order of a micrometer [22-23].

Flotation has been used as gravimetric concentration of sulphide ores for many years [24]. Depending on the different aspects of the gold in the ore, flotation can be used efficiently based on gold's high density [25]. This method is used to recover gold when the grades are extremely low. The advantages of this method over others include the simplicity of the process and equipment, as well as lower investment and operating costs [26]. The amalgamation process relies on metallic gold's ability to combine with mercury to form heat decomposable amalgams. Amalgamation is commonly regarded as a dissolution phenomenon. The mercury in the amalgam is vaporized in a furnace, condensed by distillation, and then recovered and recycled [27]. Gold digestion by mercury is possible under certain conditions: the process is only applicable in the presence of water, if the metal surfaces are clean, and if harmful impurities are not present. When the proportion of gold reaches 10 to 12%, the amalgam gradually solidifies [28-29].

Furthermore, roasting is used as a pre-treatment method for the oxidation of ores and sulphide concentrates in the pyrometallurgical concentration method. Sulphide is converted into sulphur dioxide SO_2 during oxidative roasting, which is volatilized with arsenic, and iron precipitates as hematite Fe_2O_3. Although roasting is the only method for completely removing the carbonaceous material, uncontrolled temperature and oxygen pressure conditions can result in the formation of char in the calcine, which is even more active than the original carbonaceous material [30-32].

The hydrometallurgical concentration method is used in addition to the gravimetric and pyrometallurgical concentration methods. Gold extraction metallurgy is carried out in several stages. The ore is crushed and leached in cyanide solution before being purified and recovered through adsorption on activated carbon [33-35].

The Elsner reaction describes the overall gold cyanidation mechanism [36].

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^- \tag{1}$$
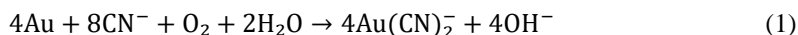
This equation emphasizes the importance of oxygen in the formation of an aurocyanide complex from metallic gold and cyanide.

Furthermore, electrolysis is the final step in the gold extraction process. The Auride ion (Au^+) is deposited at the cathode after absorbing an electron to become metallic gold [37]. The reduction and oxidation reactions respectively, are as follows:

$$2\,Au(CN)_2^- + 2e^- \rightarrow 2Au^\circ + 4CN^- \tag{2}$$

$$2OH^- \rightarrow \tfrac{1}{2}\,O_2 + H_2O + 2e^- \tag{3}$$
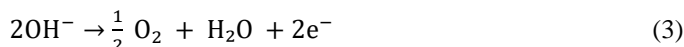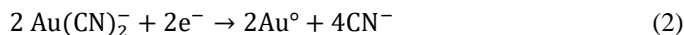
After the electrolysis operation, the cake obtained in the filter press is fused with fluxes in an oven before being poured into brick moulds. Even if some of the copper is removed during the melting process, another refining step is required to obtain pure gold [38-39].

Several processes have been initiated in recent years to permanently eliminate the use of mercury and cyanide, two toxic reagents with high health risks and environmental consequences.

In terms of gold dissolution kinetics, extraction percentage, and lower environmental and health impact, the thiourea ($CS(NH_2)_2$) process is a viable alternative to cyanide [40]. The following reaction (Eq. (4)) translates the phenomenon.

$$Au + CS(NH_2)_2 \rightarrow Au(CS(NH_2)_2)_2^+ + e^- \tag{4}$$
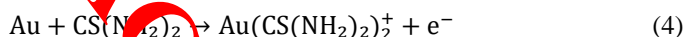
The thiosulphate process is another option for cyanidation implementation. These ions are less toxic than cyanide ions, and they allow gold to dissolve effectively in the presence of oxygen and an alkaline medium. Gold dissolves relatively slowly. It can be sped up by using catalysts (copper, ammonia) [41]. The following reaction translates the phenomenon.

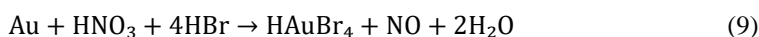$$2Au + 12O_2 + 4(S_2O_3)^{2-} + H_2O \rightarrow 2Au(S_2O_3)_2^{3-} + 2OH^- \tag{5}$$

Another well-known process is the aqua regia process. Depending on the operating conditions, extraction rates can reach 100% in hours. Because aqua regia is a corrosive and unstable reagent, it can dissolve other noble metals such as platinum and rhodium, it is used to attack gold alloys [10-12]. The following reaction shows the dissolution of water thanks to aqua regia.

$$Au + HNO_3 + 4HCl \rightarrow HAuCl_4 + NO + 2H_2O \tag{6}$$
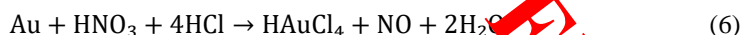
In this work, gold was leached using modified aqua regia (MAR) where hydrobromic acid (HBr) has been used for gold digestion instead of HNO_3, due to the fact that gold bromide ion and α-cyclodextrin have a good molecular recognition. The Eqs. involved by leaching process are following:

$$HNO_3 + 3HBr \rightarrow HAuBr_4 + NO + 2H_2O \tag{7}$$

$$2Au + 2Br^- + 3Br_2 \rightarrow 2AuBr_4^- \tag{8}$$
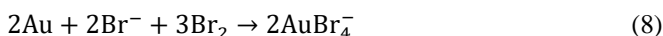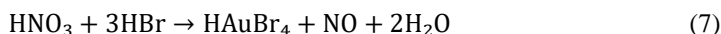
Then Eq. (6) can be written as following:

$$Au + HNO_3 + 4HBr \rightarrow HAuBr_4 + NO + 2H_2O \tag{9}$$

The other process is that with chitosan ($C_6H_{11}NO_4$), in which the latter is a polysaccharide high in amines and hydroxyl groups with a high capacity for metal ion chelation. According to the following Eq. (10), recent research has shown that chitosan can form complexes with gold after prior dissolution by chlorination [42-43].

RETRACTED PAPER on request of the authors regarding intellectual property rights issues.

AN ENVIRONMENTALLY BENIGN APPROACH FOR GOLD RECOVERY FROM GOLD...

$$2Au + 2KClO_3 + 8HCl + CS \rightarrow 2AuCl_4 - CS + 2KCl + 4H_2O + O_2 \qquad (10)$$
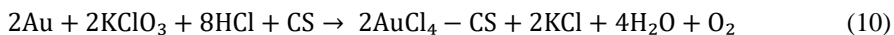
The manipuera process uses a liquid by-product of cassava flour production (manipuera) to generate hydrogen cyanide via the hydrolysis of cyanogenic glycosides as a defence mechanism against intruders [44]. The following Eq. (11) translates the phenomenon.

$$4Au + 8CN^- + O_2 + H_2O \rightarrow 4Au(CN)_2 + 4\,OH^- \qquad (11)$$
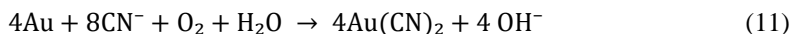
The cyclodextrin method has been used for more than a century [45]. Cyclodextrins are cyclic oligosaccharides formed by the enzymatic breakdown of starch. Their three-dimensional structure resembles a truncated cone with hydroxyl groups on the outside; as a result, the outer part is highly hydrophilic [46]. They are unique in that they can accommodate (via reversible inclusion) other molecules (solid, liquid or gaseous) in the cavity they delimit (1.5nm×0.7nm×0.8nm), resulting in the formation of super-molecules (association complexes). The inclusion complexes formed by cyclodextrins and a wide range of hydrophobic host molecules in aqueous media are largely due to the presence of this apolar cavity [47].

Inclusion-predisposing parameters are typically hydrophobic in nature and involve a variety of combined interactions, such as van der Waals interactions [48]. The following Fig. 1 shows the different structures of cyclodextrin.

The main physio-chemical characteristics of α, β and γ cyclodextrins are collated in the following table 1. Studies have shown that cyclodextrins are less-toxic, relatively low cost, biocompatible and biodegradable [49, 52].

In the Democratic Republic of Congo (D.R.C.), mining industries are involved in the extraction of a variety of materials such as copper, cobalt, iron, diamond, tin, gold, and so on [53]. Gold is mainly present in the eastern part (South-Kivu and Orientale provinces). Even on a small scale, exploited by artisanal means, the deposits remain very productive.
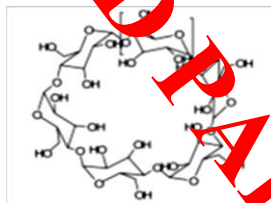
n=1, 2, 3 for α, β, γ cyclodextrins respectively

Fig. 1. Structures of cyclodextrins [49]

Moreover, even if the investment in equipment is relatively modest, the exploitation is done at a very high rate of return [54].

The mining of gold is more traditional than industrial. Diggers, also known as artisanal miners, are in charge of extracting minerals from mines, often using only their bare hands and rudimentary tools [23].

Surface mining is a type of mining in which the ore deposit extends deep underground, necessitating the removal of overburden and ore layers [55-56].

Underground mining is used for deep deposits, or mineralization that is more than a hundred meters deep. Artisanal or traditional mining refers to any type of mining that involves extracting and concentrating mineral substances as well as recovering marketable products using manual and traditional methods and processes (the direct use of human energy in mineral extraction) [57-58].

Tab. 1. Physio-chemical characteristics of cyclodextrins [50-51]

	α-cyclodextrin	β-cyclodextrin	γ-cyclodextrin
Glucose units number	6	7	8
Brute formula	$C_{36}H_{60}O_{30}$	$C_{42}H_{70}O_{35}$	$C_{48}H_{80}O_{40}$
Molecular weight (g.mol^{-1})	972	1135	1297
Solubility in water (g.L^{-1})	145	18.5	232
Ø cavity (Å) (small face-large face)	4.3-5.3	6.0-6.5	7.5-8.3
Cone height (Å)	7.9±0.1	7.9±0.1	
Approximate cavity volume (Å^3)	174	262	
Average number of water molecules	6–8	12	

In the majority of artisanal gold mining regions in the D.R.C., artisanal gold miners use mercury, despite the performance and environmental risks that it can cause. Operators are unaware of the high levels of mercury found in soil and rivers near mine sites, as well as in homes and warehouses where mercury is burned. The open burning of amalgam in small communities as well as urban areas poses the greatest health risk to miners, women, and children. As a result, there is a serious issue of environmental pollution.

The purpose of this paper is to apply α-CD to gold ores from the Kimpese quarry in the territory of Kambove, in the province of Haut Katanga in the Democratic Republic of the Congo, as an alternative to artisanal techniques with very high health risks.

Materials and methods

Materials

All analytical grade chemical reagents were used in this work, and all stock solutions were made with distilled water. Stratified sampling was used to collect gold ore samples from pits already dug by artisans. The ore from Kimpese quarry, Kambove territory, in the Haut-Katanga province of D.R.C., was sampled. To create the initial sample, systematic sampling was carried out in each area and a total of 20 kg was homogenised using the cone and crown method, which consists of forming a crown followed by a cone. This procedure was repeated six times. The quartering technique was used to divide the sample into four representative parts, which were then mixed together. The repetition of this operation allowed the representative sample for the experiments to be obtained.

Sample preparation

The total amount of collected sample (20 kg) was fragmented with a sledge hammer to a size acceptable by the laboratory jaw crusher (primary). Then the sample was crushed in a laboratory cylindrical crusher (secondary). After primary crushing, 1 kg was sorted out for AAS/inductively coupled plasma (ICP) assay, and the remaining 19 kg gold ore sample was fragmented with a laboratory jaw crusher, and then with a laboratory cylindrical crusher for 10 minutes in order to get 80% passing 75 μm sieve.

Precious metal characterization

To characterize the precious metal (gold), the AAS method with a graphite furnace HGA (high graphite atomization) 700 was used. Furthermore, a tube with an autosampler AS-70 was used to receive samples, and the calibration curve was established by preparing solutions (20, 40, 60, and 80 ng Au/cm3) in argon current using a nickel matrix modifier. To obtain good gold signals, a graphite furnace with a temperature stabilized platform-STPF was chosen [59].

Process block for gold recovery

A number of tests were used in order to recover most gold from ore sample. Among them are leaching, neutralization, and gold recovery using α-CD. In addition, some physicochemical

parameters were also studied in order to find the optimum conditions for maximum recovery. In order to better analyze the different influences of the physicochemical parameters on the leaching, neutralization, and gold recovery processes, and to design the experiments; Minitab and OriginPro software were used.

Leaching tests for precious metal recovery

The leaching process was done by mixing 450 g of the gold ore sample with MAR (900 ml) for 24 h in a 1 L beaker for 5 min of reaction time. The stirrer was used to mix the leaching solution at specific speed during the experiments. The gold ore concentrate ($HAuBr_4$), named digestate, was obtained after digestion in MAR followed by filtration. The filtrate containing valuable metal was then collected for the preparation to further experiments. The cake was washed and oven dried for 24 hours at 105°C and the concentration of gold metal in the leaching solutions was determined by AAS/ICP. Each leaching test was done in duplicate and the average value was considered. The following Eq. (12) was used to determine the leaching percentage.

$$\text{Recovery } (\%) = \frac{P_1 T_1 - P_2 T_2}{P_1 T_1} \times 100 \tag{12}$$

where: P_1: weight of dry ore to be leached

P_2: weight of dry residue obtained from leaching (cake)

T_1: content of the element in the ore to be leached

T_2: content of the element in the cake

Four factors were studied: time (x_1), HBr concentration (x_2), pH (x_3) and stirring speed (x_4). Table 2 shows the variables, codes, and symbols of the full factorial design in actual values. Thus, three levels were considered for each factor, and 27 acid leaching tests were therefore carried out by simultaneously varying the levels of each factor. The laboratory scale of leaching is shown in Fig. 2 below.

Tab. 2. Codification and levels used for leaching process

Variables	Time (hours)		HBr concentration (g/l)		pH		Stirring speed (rpm)	
Symbols	x_1		x_2		x_3		x_4	
	Level	Code	Level	Code	Level	Code	Level	Code
Code and level	2	1	80	1	1	1	400	1
	4	2	120	2	1.5	2	600	2
	6	3	160	3	2	3	800	3

After the leaching, neutralization test was carried out to prepare the reaction medium for the process of the extraction with α-CD.

Fig. 2. Lab scale leaching

Neutralization tests

The dissolved gold solution from leaching was split into aliquots of 50 ml each and put in a 500 ml beaker. The solution was then neutralized with potassium hydroxide KOH (1.0 M) to achieve the required pH values, and filtered to remove any present insoluble silver bromide or other base metals. After filtration, the solution was analyzed in order to determine the optimum value for neutralization. Each test was done in duplicate and the average value was considered. Three factors were studied: time (x_1), KOH concentration (x_2), and pH (x_3), with appropriate combination. Table 3 shows the variables, codes and symbols used for the full factorial design.

Tab. 3. Codification and levels used for neutralization process

Variables	Time (hours)		KOH concentration (M)		pH	
Symbols	x_1		x_2		x_3	
	Level	Code	Level	Code	Level	Code
Code and level	2	1	1	1	4	1
	3	2	1.5	2	5	2
	6	3	2	3	6	3

The role of neutralization was thus to find the time required to get rid of impurities that could contaminate the concentrate after leaching.

Gold recovery using α-cyclodextrin

The neutralized solution obtained (KAuBr₄) was split into aliquots of 30 ml each, and put into a 200 ml beaker, and then α-CD at the required amount was progressively added to the solution. Also the room temperature was considered. The formation of the potassium tetrabromoaurate alpha-cyclodextrin complex called recovered gold (α•Br) accelerated the co-precipitation process, also, and the co-precipitates were removed by filtration. Three factors were studied: time (x_1), α-CD concentration (x_2), and pH (x_3), with appropriate combination. Variables, codes and symbols used for the full factorial design are shown in Table 4.

Tab. 4. Codification and levels used for neutralization process

Variables	Time (minute)		α-CD concentration (g/l)		pH	
Symbols	x_1		x_2		x_3	
	Level	Code	Level	Code	Level	Code
Code and level	15	1	4.643	1	4	1
	30	2	9.286	2	5	2
			13.929	3	6	3

After filtration, α•Br was dispersed into water and then reduced with sodium bisulfite Na₂S₂O₅ to give the recovered gold metal as a precipitate in order to liberate the encapsulated gold from the early formed inclusion complex. After that, the decantation of the aqueous solution was used to collect the recovered gold metal. The recovered gold was then characterized using AAS. Each gold recovery test was done in duplicate and the average value was considered.

Experiment's design and data analysis

Minitab software was used to analyze the reliability of the results after comparing the predicted and actual responses in the leaching, neutralization, and gold recovery processes. Furthermore, the regression method was used to statistically analyze experiment results. The obtained equation was then used to calculate the predicted responses. The evaluation of the statistical parameters was done using analysis of variance (ANOVA) as a statistical analysis. For modeling and optimization, the response surface methodology (RSM), a statistical and mathematical technique, was used [60]. Then, as an alternative to factorial, second-order models

RETRACTED PAPER on request of the authors regarding intellectual property rights issues.

AN ENVIRONMENTALLY BENIGN APPROACH FOR GOLD RECOVERY FROM GOLD...

were constructed using central composite rotatable design (CCRD). The experiments in this paper were designed using CCRD, and the general equation form (Eq. 13) was considered assuming that all variables are measurable.

$$y = f(x_1, x_2, x_3, ..., x_i) \qquad (13)$$

where y is the dependent variable and x_i the independent variables.

Because model significance is an important indicator, the Fisher's F-test ANOVA was used to assess the effects of the parameters studied as well as their interactions. A non-significant variable or interaction was identified by a P-value greater than 0.05 and its 95% confidence intervals. Furthermore, a P-value less than 0.0001 indicated a highly significant variable or interaction.

The recovery procedure from sampling of Kimpese querry using α-CD is shown in Fig. 3.
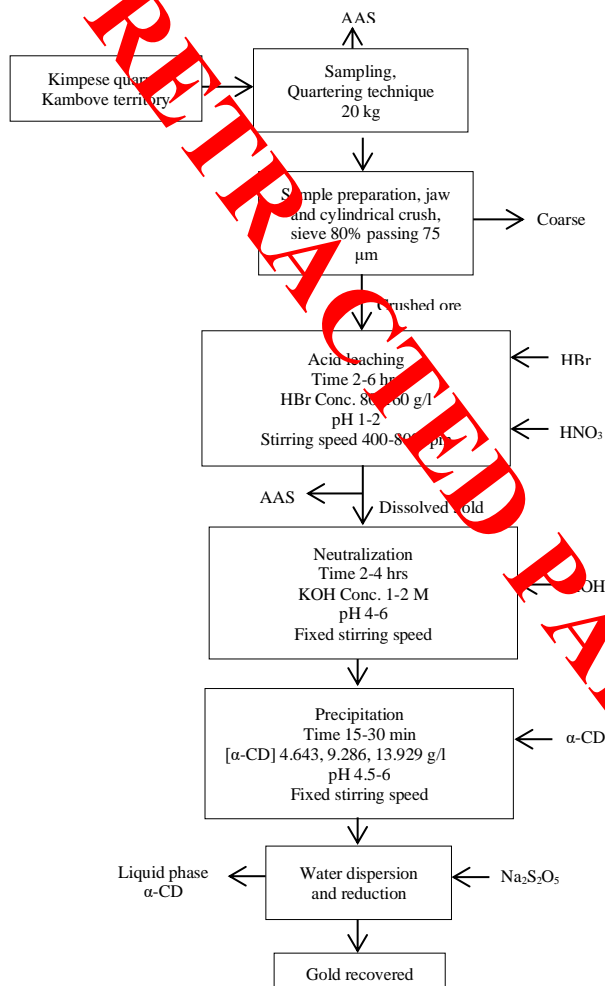

Fig. 3. Full process used for gold recovery

According to Muanda and Omalanga [60], and Liu and Wang [61], the coefficient of determination, R^2, evaluates the fitness of the found modeling equation and gives an indication about the model response could vary. R^2 value should be at least 0.80 for a good fit of a model.

Moreover, the coefficient of variation (CV) indicates the degree of precision with which the treatments are compared. When the CV value is high, the degree of dispersion around the mean value is high, while it is low when the CV is low (precision of estimation) [62].

The regression equation, which shows the effect of various factors and their interactions on the responses, was used to generate a graphical representation of the results. Using OriginPro software, this representation was created with a three-dimensional (3D) response surface and two-dimensional (2D) contour plots [60]. Those plots provided information on the variables and their interactions on the responses based on the model equations discovered in each process. Furthermore, because the leaching process model contained four variables, only two variables were used for plot representation, while the other two variables were held at the center level. Meanwhile in neutralization and gold recovery with α-CD processes, as the models have three variables, only one remaining variable was held constant at the center level.

Results and discussion

Results from the characterization to gold recovery using α-CD through some variables studies are presented and discussed in the following sections.

Characterization of the precious metal

The analyses were carried out at the metallurgical laboratory of the Ruashi mining company as well as at Congolese Control Office (Office Congolais de Contrôle) laboratory. Table 5 displays the results of the AAS/ICP analysis of the sample, which revealed the presence of other metals in addition to gold (in which this paper focuses).

Tab. 5. Chemical composition of Kimpese gold ore (Ruashi Mining Metallurgical Lab)

Metal	Al	Co	Cu	Au	Cr	Co	Mg	Fe	Si
Content (%)	2.94	0.61	0.14	0.08	0.02	0.61	2.35	5.3	13.72

Leaching tests

In this work, the room temperature was used for all the tests and after digestion process, leaching percentage was calculated. The results of the various leaching tests carried out the model established by the Minitab software are given in table 6.

Eq. (14) gives the mathematical model that represents a second order polynomial.

$$y = f(x_1, x_2, x_3, x_4) \tag{14}$$

where y represents the response (leaching percentage in %)

x_1, x_2, x_3 and x_4 represent time, HBr concentration, pH and stirring speed respectively.

From the results of table 6, the following equation was obtained by regression analysis for leaching percentage:

$$y = 71.9 + 32.21x_1 + 1.148x_2 - 226.6x_3 + 0.0304x_4 - 0.318x_1^2 - 0.00075x_2^2 + 70.7x_3^2 - 0.000013x_4^2 - 0.2220x_1x_2 + 0.00156x_1x_4 - 0.000017x_2x_4 - 0.0024x_3x_4 \tag{15}$$

Table 7 shows ANOVA and remarks of leaching process.

Tab. 6. Results of responses for leaching process

Run	Code level of variable				Leaching percentage
N_0	x_1	x_2	x_3	x_4	(%)
1	1	1	1	1	37.4
2	1	1	1	2	43.5
3	1	1	1	3	49.4
4	2	2	2	1	46.8
5	2	2	2	2	48.6
6	2	2	2	3	50.7
7	3	3	3	1	40.8
8	3	3	3	2	51.9
9	3	3	3	3	53.8
10	1	2	3	1	42.1
11	1	2	3	2	43.9
12	1	2	3	3	45.3
13	2	3	1	1	68.3
14	2	3	1	2	70.3
15	2	3	1	3	72.8
16	3	1	2	1	61.1
17	3	1	2	2	63.4
18	3	1	2	3	66.6
19	1	3	2	1	62.8
20	1	3	2	2	64.7
21	1	3	2	3	65.3
22	2	1	3	1	57.8
23	2	1	3	2	59.9
24	2	1	3	3	61.9
25	3	2	1	1	83.1
26	3	2	1	2	86.4
27	3	2	1	3	89.8

Tab. 7. Analysis of variance for leaching percentage

Source	df	Sum of Square	Mean Square	F-Value	P-Value Prob>F	Remarks
Model	12	4499.93	374.99	8.78	<0.0001	HS
x_1	1	1274.83	1274.83	29.86	<0.0001	HS
x_2	1	116.10	116.10	2.72	0.121	NS
x_3	1	369.75	369.75	8.66	0.011	S
x_4	1	4.75	4.75	0.11	0.741	NS
x_1^2	1	9.71	9.71	0.23	0.641	NS
x_2^2	1	8.72	8.72	0.20	0.658	NS
x_3^2	1	936.92	936.92	21.94	<0.0001	HS
x_4^2	1	1.64	1.64	0.04	0.848	NS
$x_1 x_2$	1	1892.74	1892.74	44.33	<0.0001	HS
$x_1 x_4$	1	4.69	4.69	0.11	0.745	NS
$x_2 x_4$	1	0.21	0.21	0.00	0.945	NS
$x_3 x_4$	1	0.70	0.70	0.02	0.900	NS
Error	14	597.79	42.70			
Total	26	5097.72				

Note: F: function of Fishers, df: degrees of freedom, P-value: level of significance, NS: not significant; S: significant; HS: highly significant; CV=7.9985%; R^2=0.8827; Adj. R^2=0.7822

The above Eq. (15) shows the most and considerable positive effect of x_1 for increasing leaching percentage, compared to x_2 and x_4 variables. At the same time, x_3 has a negative effect on the percentage and significant for the model, which means that the acidic medium is most desirable for the leaching process. In addition, since MAR is also consumed by other metals inside

RETRACTED PAPER on request of the authors regarding intellectual property rights issues.

M.M. MUANDA et al.

ore, an increase in its overall concentration will increase the leaching efficiency because it will dissolve more gold. According to table 7, the interaction x_1x_2 is highly significant for the leaching model. However, the results were satisfactory due to the high values of the determination coefficient (R^2=0.8827) and the adjusted determination coefficient (Adj. R^2=0.7822). The model was also highly significant, as evidenced by a P-Value less than 0.0001. The low value of the coefficient of variation also confirmed the precision and reliability of the experiments. Fig. 4 depicts the 3D response surface and 2D contour plots.
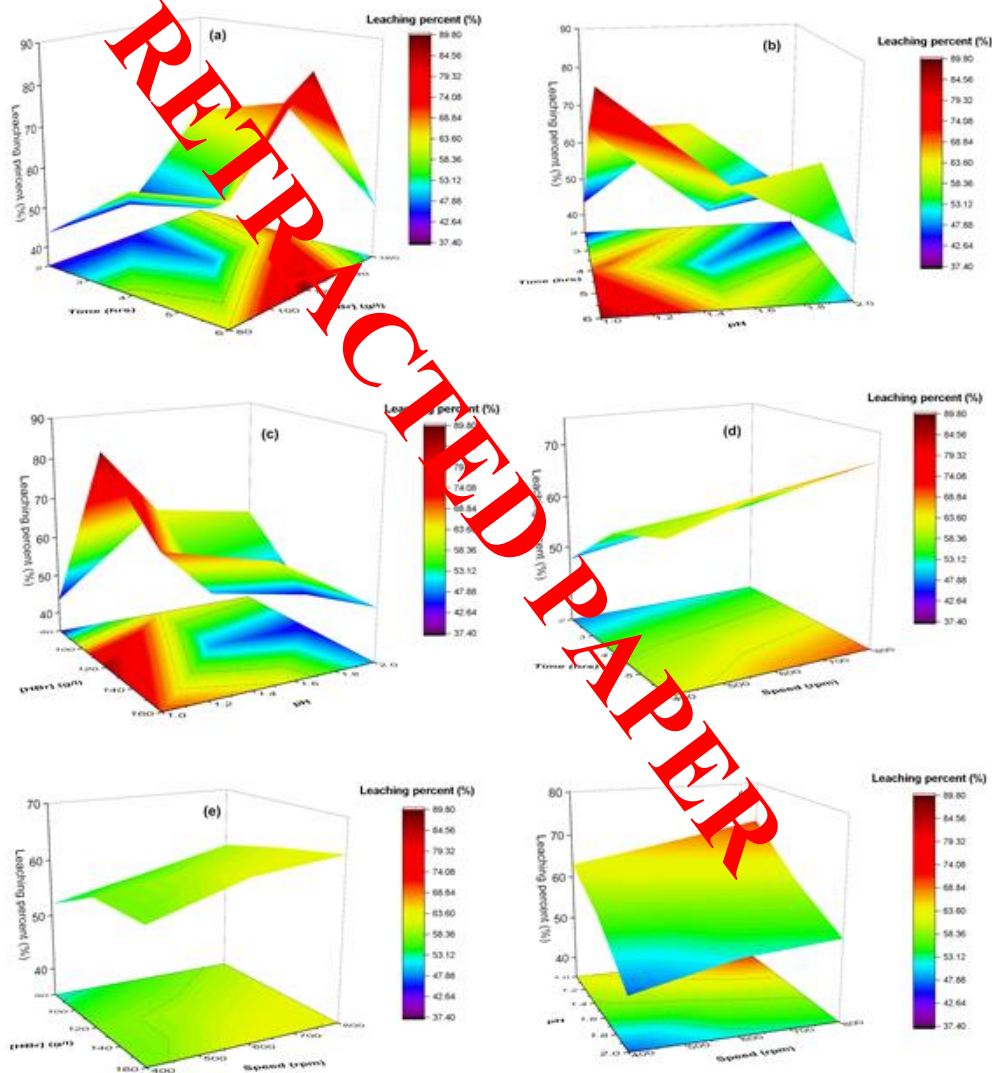

Fig. 4. Response surface plots of interaction effects on leaching percentage (other parameters are held at center level): (a) Time-[HBr]; (b) Time-pH; (c) [HBr]-pH; (d) Time-speed; (e) [HBr]-speed; (f) pH-speed

The leaching percentage is directly proportional to the increase in time and HBr concentration, and inversely proportional to that of the pH. As stated by Wei and Man [63], the presence of an oxidizing agent is required for the dissolution of gold, and in case of MAR used,

HNO_3 plays well the role of oxidant of trivalent gold ions and the ions formed are reduced by HBr followed by the formation of tetrabromidoaurate anions ($AuBr_4^-$) or tetrabromoauric acid. According to Fig. 4, reaction time had big positive effect on the leaching of gold.

Figs 4.a) and 4.b) show that time plays an important role in leaching. The percentage of 79% is obtained around a reaction time of 5 hours, thus confirming the fact that the time is directly proportional to the recovery of the gold. In addition, it is noted that for the time-HBr concentration interaction, the red triangle area is the most desirable because of a large part of recovered gold. On the other hand, in the low time zone, the value of HBr concentration has no influence on the yield for the following reasons:

- The contact between the gold particles and the leachate is not sufficient.
- HBr concentration consumes other metals present in solution under the same conditions, and this is shown by the blue and green area in Figs 4.a) and 4.c).

Concerning the HBr concentration, Figs 4.a) and 4.c) show that it is obvious that 80% of gold is recovered when the concentration of HBr is around 90 g/l confirming that the increase in the concentration of HBr leads to the increase in the production of $AuBr_4^-$ ions (Eq. (8)). On another hand, the increase in leaching percent could be explained by the formation of silver bromide (AgBr) which prevents the dissolution of silver from the aqua regia [64].

From time-pH interaction, it appears that the reduction in the acidity of the medium leads to a significant reduction in the leaching yield whatever the reaction time. Moreover, when the contact time low, less is the amount of gold recovered which confirms the result from time-HBr concentration interaction. In addition, the red zone (desired) is more visible in the time range of 4-6 hours and pH of 1-1.35.

The HBr concentration-pH interaction confirms that HBr concentration is inversely proportional to pH. The yield is obtained at its greatest value when the pH is around 1 and the HBr concentration around 120 g/l. Figs 4.d), 4.e) and 4.f) show that there was no significant change in the leaching percentage of the metals within the stirring speed indicating that the leaching reaction is not under the mass transfer control [64]. However, when the reaction rate is in the range of 600-800 rpm, the red zone is visible only in time-speed and pH-speed interactions.

The optimization has been done to find the better condition of the leaching process with the highest percentage with the minimum values of studied parameters. Optimum conditions were predicted by RSM method and results are shown in table 8.

Tab. 8. Optimization of leaching percentage

Case	Target	Time (hours)	[HBr] (g/l)	pH	Stirring speed (rpm)	Leaching percent (%)	Desirability
Leaching percent Variables	Maximum Minimum	6	80	1	800	98.6928	1

From the results of the above table 8, it is seen that by carrying out an oxidizing acid leaching of the ore treated under conditions such as: time of 6 hours, concentration of HBr of 80 g/l, pH of 1 and the stirring speed of 800 rpm; there is a 95% chance that the leaching percentage is 98.6928%. Those conditions were retained and used for the further experiments. Taking into account the leaching test by considering the optimized parameters, the gold content obtained in the filtrate was 4643 ppm.

Neutralization tests

During the experiments, the room temperature was used for all the tests. From the model established by the Minitab software, the results are given in table 9. Regression analysis was used to obtain the following equation for neutralization percentage from the results of table 9:

RETRACTED PAPER on request of the authors regarding intellectual property rights issues.

M.M. MUANDA et al.

$$y = -130.0 + 14.40x_1 - 52.20x_2 + 69.43x_3 - 1.733x_1^2 + 3.067x_2^2 - 4.167x_3^2 + 15.13x_1x_2 - 4.100x_1x_3 \qquad (16)$$

where y represents the response (leaching percentage)

x_1, x_2 and x_3 represent time, KOH concentration, and pH respectively.

The above Eq. (16) shows the most dependence of x_3 and x_1 on the neutralization percentage. According to results of 3D response surface and 2D contour plots shown in Fig. 5 below, it is obvious that the time is directly proportional to the pH and the KOH concentration in increasing neutralization percent.

Tab. 9. Results of responses for neutralization process

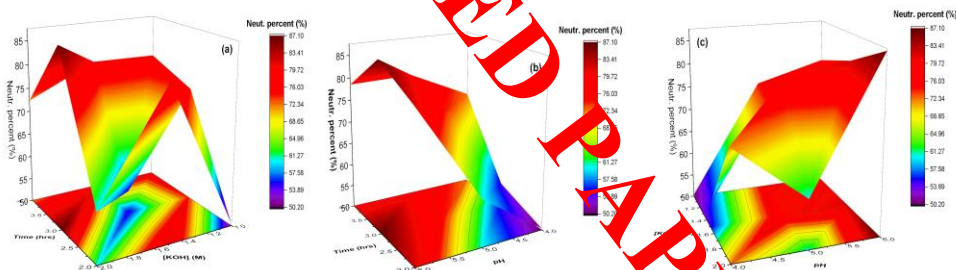| Run N_0	Code level of variable			Neutralization percentage (%)
	x_1	x_2	x_3	
1	1	1	1	50.3
2	2	2	1	54.7
3	3	3	1	72.3
4	2	1	2	74.4
5	3	2	2	78.8
6	1	3	2	60.3
7	3	1	3	78.5
8	1	2	3	81.8
9	2	3	3	87.1

Fig. 5. Response surface plots of interaction effects on leaching percentage (other parameters are held at center level): (a) Time-[KOH]; (b) Time-pH; (c) [HBr]-pH

According to Fig. 5, it is obvious that the red zone (87% yield) is in the time range of 2.30-3.75 and the pH range of 5.75-6, tending to the dark red zone when the pH tends towards 5.5-6 values. This can be explained by the fact that the other metals that accompany gold precipitate with increasing pH or KOH concentration. In view of the results of table 5, iron, aluminum, copper, cobalt, etc. are present in the ore. Thus, some of these metals are dissolved during leaching by MAR, HNO_3 and HBr, so those metals are in solution in the form of ions. During neutralization with KOH, these metals are precipitated according to Eqs. 17, 18, 19, followed by the increase of the yield.

$$Al^{3+} + OH^- \rightarrow Al(OH)_3 \qquad (17)$$

$$Cu^{2+} + OH^- \rightarrow Cu(OH)_2 \qquad (18)$$

$$Fe^{3+} + OH^- \rightarrow Fe(OH)_3 \qquad (19)$$

Moreover, the precipitation of aluminum was performed in the pH range from 4 to 5.5. While the precipitation of copper was carried out and started to precipitate at pH=4 with a total precipitation at pH 6. In the case of iron, precipitation could be caused by the progressive oxidation of Fe^{2+} to Fe^{3+} by oxygen in the air and its precipitation in the form of $Fe(OH)_3$, which began at pH 3.5 [65].

Gold recovery using α-CD tests

In this section, room temperature and pH range of 4.5-6 were considered. In addition, time and α-CD ratio ranges were 15-30 minutes and 4.643-13.929 g/l respectively. Fig. 6 below shows the solution states before and after extraction by α-CD.
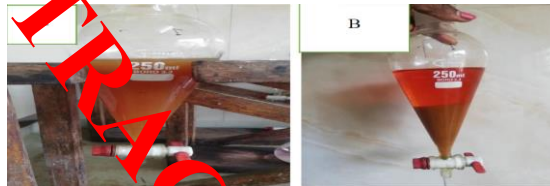

Fig. 6. Mixed solution containing gold (A): before separation, (B): after separation

From the model established by the Minitab software, the results are given in table 10.

Tab. 10. Results of responses for gold recovery with α-CD

Run N_0	Code level of variables			Gold recovery (%)
	x_1	x_2	x_3	
1	1	1	1	2.93
2	1	2	1	57.07
3	1	3	1	49
4	2	1	1	67.3
5	2	2	1	87.27
6	2	3	1	82.
7	1	1	2	42.33
8	1	2	2	64.47
9	1	3	2	60.6
10	2	1	2	77.89
11	2	2	2	83.65
12	2	3	2	80.6
13	1	1	3	64.78
14	1	2	3	77.69
15	1	3	3	77.25
16	2	1	3	85.02
17	2	2	3	87.39
18	2	3	3	76.41

The following Eq. (20) was obtained from the results of table 10 by regression analysis for gold recovery.

$$y = -237 \; + 7.53x_1 + 16.31x_2 + 41.3x_3 - 0.466\,x_2^2 - 0.01x_3^2 - 0.0853\,x_1x_2 - 1.015\,x_1x_3 - 0.922x_2x_3 \tag{20}$$

where y represents the response (leaching percentage)

x_1, x_2 and x_3 represent time, α-CD ratio, and pH respectively.

The above Eq. (20) shows the most and significant effects of all the parameters. ANOVA results are presented in table 11.

Tab. 11. Analysis of variance for gold recovery

Source	df	Sum of Square	Mean Square	F-Value	P-Value Prob>F	Remarks
Model	8	4178.54	522.32	34.10	<0.0001	HS
x_1	1	1970.87	1970.87	128.66	<0.0001	HS
x_2	1	205.50	205.50	13.41	0.005	S
x_3	1	653.28	653.28	42.64	<0.0001	HS
x_2^2	1	403.61	403.61	26.35	0.001	S
	1	0.00	0.00	0.00	0.998	NS
x_1x_2	1	105.85	105.85	6.91	0.027	S
x_1x_3	1	405.44	405.44	26.47	0.001	S
x_2x_3	1	85.49	85.49	5.58	0.042	NS
Error		37.87	15.32			
Total	17	4316.41				

Note: F: function of Fishers, df: degrees of freedom, P-value: level of significance, NS: not significant; S: significant; HS: highly significant; CV=3.9597%; R^2=0.9681, adj. R^2=0.9397

According to table 11, the significance of the model is confirmed by the values of R^2=0.9681 and Adj. R^2=0.9397. Moreover, the CV value (3.9597%) confirmed the good reliability of the experiments and the precision.

The results of 3D response surface and 2D contour plots are presented in Fig. 7 below, and it is obvious that all the three parameters are significant on gold recovery percent.

It has been observed the formation of a shiny pale brown suspension within a minimum of 1 minute after the addition of α-CD solution to KAuBr$_4$ solution, showing a rapid reaction process. Liu et al. [66] and Anthony et al. [45] stated that series of two coordination spheres are considered for the transition metals during the reaction process.

It is the first coordination sphere in which hydrogen bonds to ligands exist when there is a direct bond between molecules and metal. The attachment between the molecules in the first coordination and the ions inside the charged complexes that are bonded to the first coordination is referred to as the second coordination sphere.

Furthermore, the first coordination sphere has a greater influence on metal complex reactivity and chemical properties than the second coordination sphere. Kakume et al. [49] have shown that during gold recovery process, there is encapsulation of AuBr ions with the second-sphere cavity between the primary OH faces of the repeated face-to-face α-CD pairs stabilized by the hydrogen bonding interactions.

Then the molecules K+, α-CD and AuBr4− recognize each other and correspond at the same time, which results in facilitation of a specific second-sphere coordination (involving aureate anion [AuBr$_4$] $^−$ and hexa-aqua cation [K(OH$_2$)$_6$]$^+$ interacting with each other non-covalently). According to Liu et al. [67], there is then a rapid co-precipitation of α-CD and KAuBr$_4$ in water concluded by the formation of a 1:2 ratio complex (needlelike) $\{[K(OH_2)_6][AuBr_4]\subset(\alpha\text{-}CD)_2]\}_n$. The co-precipitate formed is filtered and reduced using Na$_2$S$_5$O$_2$ to liberate the encapsulated gold from the inclusion complex. Finally the recovered gold from is characterized using AAS to calculate the percentage.

In view of Figs 7.b) and 7.d), it is noted that the time is directly proportional to the percentage of gold recovery. A recovery was observed from the first minute of reaction; however the dark red zone is reached from 27 minutes, so that a yield of at least 80% is obtained. According to Figs 7.b) and 7.f), the yield area in the 80-89% percentage range is within the range of α-CD concentration 8-12 g/l. But for high yields (at least 89%) corresponding to the dark red zone, the range of α-CD concentration decreases down to 8-10 g/l.

Considering α-CD concentration-pH interaction, a yield of at least 86% is observed when pH and α-CD concentration are 5.65 and 8.9 g/l respectively; while for pH-time interaction, the

RETRACTED PAPER on request of the authors regarding intellectual property rights issues.

AN ENVIRONMENTALLY BENIGN APPROACH FOR GOLD RECOVERY FROM GOLD...

yield is at least 80% when the pH and time are 5 and 29 minutes respectively. This is also explained by the fact that few accompanying metals of gold have been eliminated by neutralization.
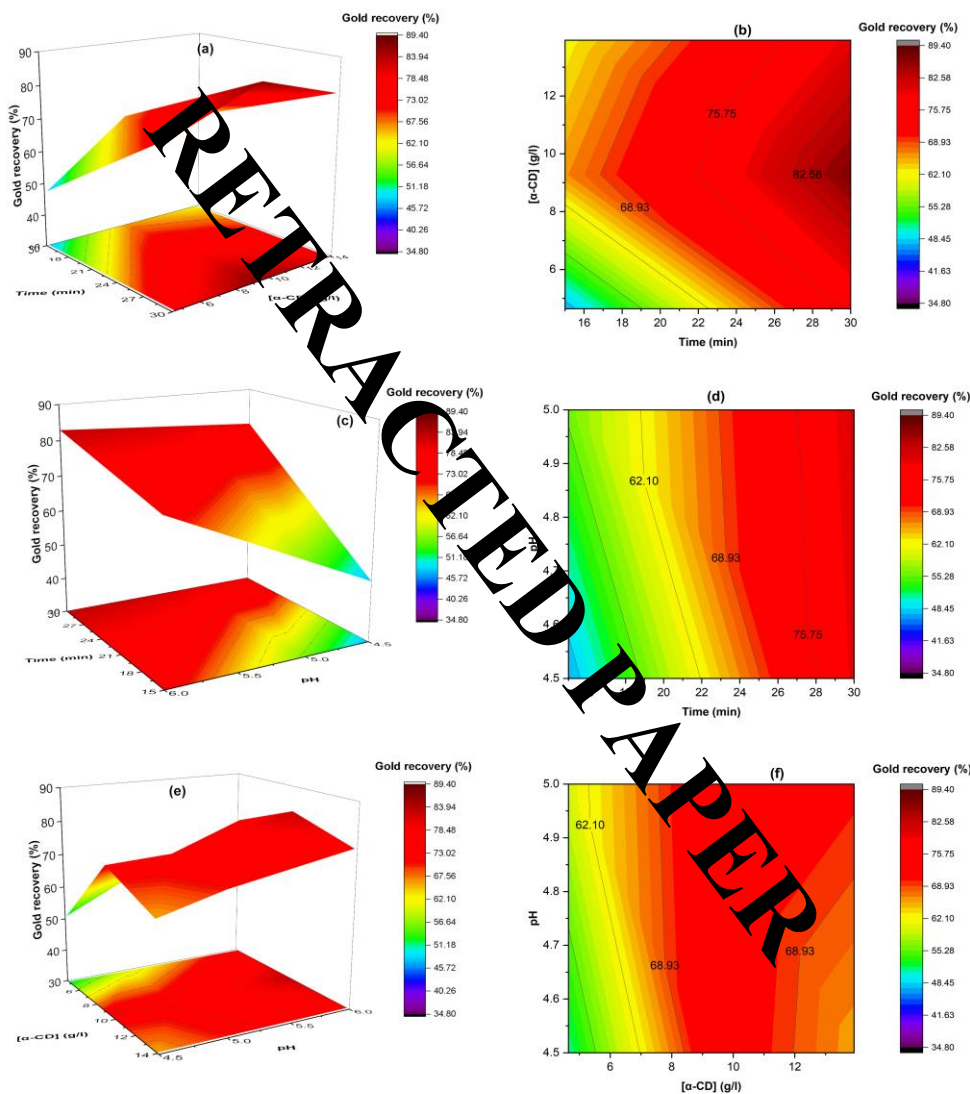

Fig. 7. Response surface plots of interaction effects on leaching percentage (other parameters are held at center level): (a), (b) Time-[α-CD]; (c), (d) Time-pH; (e), (f) [α-CD]-pH

From the results obtained in Fig. 7, it is obvious that the increase in [α-CD] leads to an increase in the percentage of recovery up to a maximum value, followed by the decrease. This can be explained by the fact that the perfect match in molecular recognition within the complex formed requires that the ratio be equal to 1:2, that is to say that $\frac{[\text{AuBr4}]}{[\alpha-\text{CD}]} = \frac{1}{2}$. Below and above this ratio, there is a percentage drop. So for better performance, the value of [α-CD] should be around twice that of [AuBr$_4$].

RETRACTED PAPER on request of the authors regarding intellectual property rights issues.

M.M. MUANDA et al.

The variation of time is also proportional to that of the percentage of recovery. On the other hand, the pH does not have a great influence in the chosen range (4.5-6), thus confirming that good neutralization has been carried out. Moreover, optimization conditions were predicted by the RSM method and results are shown in table 12.

Tab. 12. Optimization of gold recovery

Case	Target	Time (min)	[α-CD] (g/l)	pH	Gold recovery (%)	Desirability
Gold recovery Variables	Maximum Minimum	30	8.86391	6	89.7350	0.9999

From results of table 12 it appears that by working under conditions such as the time of 30 minutes, the α-CD concentration of 8.86391g/l and the pH of 6, there is a 95% chance that the gold recovery is 89.7350% with desirability equal to 0.9999. Under these conditions, the found results of analysis of obtained organic phase and raffinate by AAS were 16434 ppm and 493.25 ppm respectively, confirming the success of gold recovery process.

Conclusions

This paper aimed to find the optimal conditions for the recovery of gold from the Kimpese quarry in the Democratic Republic of Congo (D.R.C.), using alpha cyclodextrin (α-CD) technique as an alternative technique to the use of mercury. Atomic absorption spectroscopy (AAS) revealed that Kimpese gold ore deposit contains an average of 0.08% gold. Leaching, neutralization and gold extraction with α-CD tests were carried out. With regard to leaching, the following factors were varied: time (2 hours, 4 hours and 6 hours), pH (1, 1.5 and 2), HBr concentration (80g/l, 120g/l and 160g/l), and stirring speed (400rpm, 600rpm and 800rpm). According to neutralization tests, the following factors were varied: time (2 hours, 3 hours and 6 hours), KOH concentration (1M, 1.5M and 2M), and pH (4, 5 and 6). The extraction tests were carried out taking into account the following factors: time (5minutes and 30minutes), α-CD concentration (4.643g/l, 9.286g/l and 13.929g/l), pH (4.5, 5 and 6). The optimal gold extraction parameters determined by using analysis of variance (ANOVA) and response surface methodology (RSM). Yield optimization for leaching tests revealed the following optimal parameters: 6hours (time), 1 (pH), 80g/l (HBr concentration) and stirring speed (800rpm); which led to a leaching yield of 98.6928% gold corresponding to a grade of 4443 ppm. According to neutralization, the optimal parameters corresponded to the pH range of 4.5-6 for further tests. The optimal parameters for gold extraction were: 30 minutes (time), 8.8639g/l (α-CD concentration) and 6 (pH), which equals an extraction yield of 89.7350%. Gold was enriched and extracted in a single extraction stage, with a starting grade of 0.8% to a final grade of 16431 ppm after extraction with α-CD. In addition, the final content in the raffinate was 493.25 ppm. This method of recovering gold from ore using α-CD is advantageous, low-cost, and environmentally friendly.

References

[1] M.E. McHenry, M.A. Willard, D.E. Laughlin, *Amorphous and nanocrystalline materials for applications as soft magnets*, **Prog. Mater. Sci.**, **44**, 1999, pp. 291.

[2] Y. Han, C.T. Chang, S.L. Zhu, A. Inoue, D.V. Louzguine-Luzgin, E. Shalaan, F. Al-Marzouki, *Fe-based soft magnetic amorphous alloys with high saturation magnetization above 1.5 T and high corrosion resistance*, **Intermetallics**, **54,** 2014, pp. 169-175.

[3] K. Brzozka, A. Slawska-Waniewska, P. Nowicki, K. Jezuita, *Hyperfine Magnetic Fields in FeZrB(Cu) alloys*, **Material Science and Engineering A**, 226-228, 1997, pp. 654-658.

RETRACTED PAPER on request of the authors regarding intellectual property rights issues.

AN ENVIRONMENTALLY BENIGN APPROACH FOR GOLD RECOVERY FROM GOLD...

A. Inoue, *Stabilization of metallic supercooled liquid and bulk amorphous alloys*, **Acta Materialia**, **48**, 2000, pp. 279-306.

[4] M. Nabialek, K. Jez, *The Influence of the Manufacturing Method on the Structure and Magnetic Properties of Rapid Cooled Iron Based Alloys*, **Revista de Chimie**, **69(6)**, 2018, pp. 1593-1597.

[5] C. Wu, H. Chen, H. Lv, M. Yan, *Interplay of crystallization, stress relaxation and magnetic properties for FeCuNbSiB soft magnetic composites*, **Journal of Alloys and Compounds**, **673**, 2016, pp. 278-282.

[6] T. Janta, *Wpływ temperatury pracy na właściwości magnetyczne dielektromagnetyków*, **Zeszyty problemowe – Maszyny Elektryczne**, **75**, 2006, pp. 171-175.

[7] C. Xia, Y. Peng, L. Yi, H. Deng, Y. Zhu, G. Hu, *The magnetic properties and microstructure of phosphated amorphous FeSiCr/silane soft magnetic composite*, **Journal of Magnetism and Magnetic Materials**, **474**, 2019, pp. 424–433.

[8] M. Nabiałek, K. Bloch, M. Szota, A.V. Sandu, *Structure and Magnetic Properties of Composite Toroids Powder Casted*, **Materiale Plastice**, **54(3)**, 2017, pp. 491-494.

A. Muezzinoglu, *A Review of Environmental Considerations on Gold Mining and Production,* **Critical Reviews in Environmental Science and Technology, 33**, 2003, pp. 45-71. https://doi.org/10.1080/10643380390814451.

[9] C.R.M. Butt, R. Hough, M. Verrall, *Gold nuggets: the inside story,* **Ore and Energy Resource Geology**, **4–5**, 2020, 100009, ISSN 2666-2612. https://doi.org/10.1016/j.oreoa.2020.100009.

[10] F. Robert, R. Brommecker, B. Bourne, P.J. Dobak, C. Mcewan, R.R. Rowe, X. Zhou, *Models and exploration methods for major gold deposit types*, **Proceedings of Exploration 07: Fifth Decennial International Conference on Mineral Exploration,** 2007, pp. 691-711.

[11] M. M. Muanda, P. P. D. Omalanga, V.M. Mitonga, *Comparative Cleaning Stages in Recovery of Copper and Cobalt from Tailings using Potassium Amylxanthate as Collector*, **European Journal of Engineering and Technology Research, 6(2),** 2021, pp. 96–100. https://doi.org/10.24018/ejeng.2021.6.2.2165.

[12] M. Mukunga, *Recovery of copper and cobalt in the comparative flotation of a sulfide ore using xanthate and dithiophosphate as collectors*, **International Journal of Engineering and Applied Sciences (IJEAS), 6(7),** 2019, pp. 26-29. https://dx.doi.org/10.31873/IJEAS.6.7.2019.06.

[13] I.V. Gas'kov, *Major impurity elements in native gold and their association with gold mineralization settings in deposits of Asian folded areas*, **Russian Geology and Geophysics, 58,** 2017, pp. 1080-1092. https://dx.doi.org/10.1016/j.rgg.2017.08.004.

[14] N. Weiher, E. Bus, L. Delannoy, C. Louis, D.E. Ramaker, J.T. Miller, J. Bokhoven, *Structure and oxidation state of gold on different supports under various CO oxidation conditions*, **Journal of Catalysis, 240**, 2006, pp. 100-107. https://dx.doi.org/10.1016/j.jcat.2006.03.010.

[15] J. Lin, S. Zhang, W. Guan, G. Yang, Y. Ma, *Gold with +4 and +6 Oxidation States in AuF4 and AuF6*, **Journal of the American Chemical Society, 140**, 2018, pp. 9545–9550. https://dx.doi.org/10.1021/jacs.8b04563.

[16] H. Klimev, K. Fajerwerg, K. Chakarova, L. Delannoy, C. Louis, K. Hadjiivanov, *Oxidation of gold metal particles supported on TiO2: An FTIR study by means of low-temperature CO adsorption,* **Journal of Materials Science, 42,** 2007, 3299-3306. https://dx.doi.org/10.1007/s10853-006-0777-1.

RETRACTED PAPER on request of the authors regarding intellectual property rights issues.

M.M. MUANDA et al.

[17] P. Cyganowski, K. Garbera, A. Leśniewicz, J. Wolska, P. Pohl, D. Jermakowicz-Bartkowiak, *The recovery of gold from the aqua regia leachate of electronic parts using a core–shell type anion exchange resin,* **Journal of Saudi Chemical Society, 21,** 2017. https://dx.doi.org/10.1016/j.jscs.2017.03.007.

[18] R. Grayson, Fine *Gold Recovery – Alternatives to Mercury and Cyanide Purpose of study*, **World Placer Journal, 7,** 2007, pp. 66-161.

[19] Ya. Bonggotgetsakul, R. Cattrall, S. Kolev, *Recovery of gold from aqua regia digested electronic scrap using a poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) based polymer inclusion membrane (PIM) containing Cyphos® IL 104,* **Journal of Membrane Science, 514,** 2016. https://dx.doi.org/10.1016/j.memsci.2016.05.002.

[20] E. Demann, P. Stein, J. Haubenreich, *Gold as an Implant in Medicine and Dentistry*, **Journal of long-term effects of medical implants, 15,** 2005, pp. 687-98. https://dx.doi.org/10.1615/JLongTermEffMedImplants.v15.i6.100.

[21] J. Donaldson, *The use of gold in dentistry,* **Gold Bulletin, 13,** 2013, pp. 160-165. https://dx.doi.org/10.1007/BF03215462.

[22] H. Knosp, R. Holliday, C. Corti, *Gold in Dentistry: Alloys, Uses and Performance*, **Gold Bulletin, 36**, 2003, pp. 93-102. https://dx.doi.org/10.1007/BF03215496.

[23] J. Oleszek-Listopad, K. Sarna-Boś, A. Szabelska, E. Czelej-Piszcz, J. Borowicz, S. Jolanta, *The use of gold and gold alloys in prosthetic dentistry - A literature review,* **Current Issues in Pharmacy and Medical Sciences, 28,** 2015. https://dx.doi.org/10.1515/cipms-2015-0070.

[24] T. Ellis, *The future of gold in electronics*, **Gold Bulletin, 37,** 2004, 66-71. https://dx.doi.org/10.1007/BF03215118.

[25] P. Goodman, *Current and future uses of gold in electronics*, Gold Bulletin. 35 (2002) 21-26, https://dx.doi.org/10.1007/BF03214833.

[26] R. Holliday, P. Goodman, *Going for gold [gold in electronics industry],* **IEE Review, 48**, 2002, pp. 15–19. https://dx.doi.org/10.1049/ir:20020308.

[27] J. Schroers, B. Lohwongwatana, W. Johnson, A. Peker, *Gold Based Bulk Metallic Glass*, **Applied Physics Letters, 87**, 2005, 061912-061912. https://dx.doi.org/10.1063/1.2008374.

[28] J. Schroers, B. Lohwongwatana, W. Johnson, A. Peker, *Precious bulk metallic glasses for jewelry applications,* **Materials Science and Engineering A., 448,** 2007. https://dx.doi.org/10.1016/j.msea.2006.02.301.

[29] S. Acar, *Process development metallurgical studies for gold oxidation process*, **Minerals & Metallurgical Processing, 33,** 2016, pp. 161-171. https://dx.doi.org/10.19150/mmp.6837.

[30] K. Kongolo, M. Mwema, *The extractive metallurgy of gold*, **Hyperfine Interactions, 111,** 1998, pp. 281-289. https://dx.doi.org/10.1023/A:1012678306334.

[31] M.M. Muanda, P.P.D. Omalanga, *Influence of Lead Nitrate on Sulfurizing Flotation of a Copper-Cobalt Oxide Ore,* **Walailak Journal of Science and Technology (WJST), 18(10),** 2021. https://doi.org/10.48048/wjst.2021.9319.

[32] N. Singh, A rugged, *precise and accurate new gravimetry method for the determination of gold: An alternative to fire assay method,* **SpringerPlus.,** 2012, pp. 1-14. https://dx.doi.org/10.1186/2193-1801-1-14.

[33] Z.Z. Xia, *Determination of silver in gold-loaded carbon by fire assay gravimetric method*, **Yejin Fenxi/Metallurgical Analysis, 37,** 2017, 54-58. https://dx.doi.org/10.13228/j.boyuan.issn1000-7571.010052.

RETRACTED PAPER on request of the authors regarding intellectual property rights issues.

AN ENVIRONMENTALLY BENIGN APPROACH FOR GOLD RECOVERY FROM GOLD...

[34] P. Appel, L. Na-Oy, *Mercury-Free Gold Extraction Using Borax for Small-Scale Gold Miners*, **Journal of Environmental Protection, 5,** 2014, pp. 493-499. https://dx.doi.org/10.4236/jep.2014.56052.

[35] W. Brooks, H. Öztürk, Z. Cansu, *Amalgamation and Small-Scale Gold Mining at Ancient Sardis,* **Turkey, Archaeological Discovery, 5,** 2017, pp. 42-59. https://dx.doi.org/10.4236/ad.2017.51003.

[36] E.N. Maratas, *Environmental awareness and health assessment in artisanal and small-scale gold mining of sibutad*, **Zambaonga del norte,** 2020. https://dx.doi.org/10.13140/RG.2.2.31846.04163.

[37] M.W. Ojeda, E. Perino, M. Ruiz, *Gold extraction by chlorination using a pyrometallurgical process,* **Mineral Engineering-Miner Eng., 22,** 2009, pp. 409-411. https://dx.doi.org/10.1016/j.mineng.2008.09.002.

[38] R. Seisembayev, S. Kozhakhmetov, S. Kvyatkovsky, *A. Semenova, Extraction of Gold from Refractory Gold-Bearing Ores by Means of Reducing Pyrometallurgical Selection*, **Metallurgist, 64,** 2020, pp. 788-795. https://dx.doi.org/10.1007/s11015-020-01055-z.

[39] W. Anuar, M. Ardani, N. Banarun, S. Ismail, S. Rahman, *Optimization Process of the Refractory Gold Ore Extraction by Hypochlorite Oxidative Leaching, Mining*, **Metallurgy & Exploration, 38,** 2021. https://dx.doi.org/10.1007/s42461-020-00376-6.

[40] R. Radulescu, F-O. Antoneta, E. Panturu, L. Grigoraş, *New Hydrometallurgical Process for Gold Recovery,* **53,** 2008.

[41] E. Neag, E. Kovacs, Z. Dinca, A. Török, C. Varaticeanu, E-A Levei, *Hydrometallurgical Recovery of Gold from Mining Wastes*. 2020. https://dx.doi.org/10.5772/intechopen.94597.

[42] W. Xing, M-S. Lee, *Development of a hydrometallurgical process for the recovery of gold and silver powders from anode slime containing copper, nickel, tin, and zinc,* **Gold Bulletin, 52,** 2019. https://dx.doi.org/10.1007/s13404-019-0254-0.

[43] G. Deschênes, *Advances in the cyanidation of gold, Developments in Mineral Processing, 15,** 2005. https://dx.doi.org/10.1016/S0167-4528(05)15009-0.

[44] J. Ficeriová, P. Baláž, *Electrolysis of Gold from Filtration Waste by Means of Mechanical Activation,* **Acta Montanistica Slovaca, 17,** 2012, pp. 132-137.

[45] O. Hyvärinen, M. Hämäläinen, P. Lamberg, J. Liipo, *Recovering gold from copper concentrate via the HydroCopper™ process,* **JOM: the journal of the Minerals, Metals & Materials Society, 56,** 2004, pp. 57-59. https://dx.doi.org/10.1007/s11837-004-0184-5.

[46] T.H. Rehren, S. Nixon, *Refining gold with glass – an early Islamic technology at Tadmekka, Mali,* **Journal of Archaeological Science, 49,** 2014, pp. 33-41. ISSN 0305-4403. https://doi.org/10.1016/j.jas.2014.04.013.

[47] J. Li, J. Miller, *A review of gold leaching in acid thiourea solutions, Mineral Processing and Extractive Metallurgy* Review-Miner Process Extr Metall Rev. 27 (2006) 177-214, https://dx.doi.org/10.1080/08827500500339315.

[48] B. Xu, W. Kong, Q. Li, Y. Yang, X. Liu, *A Review of Thiosulfate Leaching of Gold: Focus on Thiosulfate Consumption and Gold Recovery from Pregnant Solution*, **Metals, 7,** 2017. https://dx.doi.org/10.3390/met7060222.

[49] Y-C. Chang, D-H. Chen, *Recovery of gold (III) ions by a chitosan-coated magnetic nano-adsorbent,* **Gold Bulletin, 39,** 2006, pp. 98-102. https://dx.doi.org/10.1007/BF03215536.

[50] M. Arrascue, O. Horna, E. Guibal, *Gold sorption on chitosan derivatives*, Hydrometallurgy, 71 (2003) 191-200, https://dx.doi.org/10.1016/S0304-386X(03)00156-7.

[51] P. Torkaman, M.M. Veiga, L.R.P. de Andrade Lima, L.A. Oliveira, J.S. Motta, J.L. Jesus, L.M. Lavkulich, *Leaching gold with cassava: An option to eliminate mercury use in artisanal*

gold mining, **Journal of Cleaner Production, 311**, 2021, 127531, ISSN 0959-6526. https://doi.org/10.1016/j.jclepro.2021.127531.

A. Anthony, U. Abubakar Zaria, A. Atta, S. Magaji, *Recovery of Gold from Shanono Gold Ore Deposit Using α-Cyclodextrin,* **Mining, Metallurgy & Exploration**, **37**, 2020. https://dx.doi.org/10.1007/s42461-020-00227-4.

[52] Z. Ruyue, Z. Yang, D. Xiling, S. Shiguo, L. Yingchun, *A novel dual-signal electrochemical sensor for isphenol A determination by coupling nanoporous gold leaf and self-assembled cyclodextrin,* **Electrochimica Acta, 271,** 2018, pp. 417-424, ISSN 0013-4686. https://doi.org/10.1016/j.electacta.2018.03.113.

[53] Kumar A., Ashok K., Bonthagarala B., Sreekanth Dr. N., Rao C.H., *The cyclodextrins: A review,* **2**, 2013.

[54] L. Almagro, M. Pedreño, *Use of cyclodextrins to improve the production of plant bioactive compounds,* **Phytochemistry Reviews, 19,** 2020. https://dx.doi.org/10.1007/s11101-020-09704-6.

[55] Karume, S. Tewolde, E. Tejandeke, I.Z.T. Mukasa, R. Mbabazi, *Efficiency of Crude α-Cyclodextrin in Gold Recovery from Electronic Waste and Soil,* **Green and Sustainable Chemistry, 12,** 2022, pp. 73-82. https://doi.org/10.4236/gsc.2022.123006.

[56] P. Jansook, N. Ogawa, T. Loftsson, Thorsteinn, *Cyclodextrins: structure, physicochemical properties and pharmaceutical applications,* **International Journal of Pharmaceutics, 535,** 2017. https://dx.doi.org/10.1016/j.ijpharm.2017.11.018.

[57] F. Bezerra, M. Lis, H. Firmino, J. Silva, C. Valle, J. Alexandre, B. Valle, A. Tessaro, F. Scacchetti, J. Valle, R. Valle, *The Role of β-Cyclodextrin in the Textile Industry*-Review, **Molecules, 25,** 2020, pp. 3624. https://dx.doi.org/10.3390/molecules25163624.

[58] J. Wankar, N.G. Kotla, S. Gera, S. Rasala, A. Pandit, Y.A. Rochev, *Recent Advances in Host–Guest Self-Assembled Cyclodextrin Carriers: Implications for Responsive Drug Delivery and Biomedical Engineering*, **Adv. Funct. Mater. 30,** 2020, 1909049. https://doi.org/10.1002/adfm.201909049.

[59] M.M. Muanda, H. Farag, G. Malash, *The Use of Agricultural Waste in Solving of Environmental Problems in Democratic Republic of the Congo,* **International Journal of Progressive Sciences and Technologies, 33(2)**, 2022, pp. 336-348. http://dx.doi.org/10.52155/ijpsat.v33.2.4429.

[60] J. Kilosho Buraye, N. Stoop, M. Verpoorten, *The social minefield of gold digging in South-Kivu, D.R.C. The case of Kamituga*, 2016. https://dx.doi.org/10.13140/RG.2.1.1439.0163.

[61] Mukotanyi, S. Geenen, *The future of artisanal gold mining and miners under an increasing industrial presence in South-Kivu and Ituri, Eastern Democratic Republic of Congo*, 2016. https://dx.doi.org/10.13140/RG.2.1.2194.0885.

[62] S. Geenen, Constraints, O*pportunities and Hope: Artisanal Gold Mining and Trade in South-Kivu (D.R.C),* 2011. https://dx.doi.org/10.1057/9780230304994_10.

[63] J. Kilosho Buraye, N. Stoop, M. Verpoorten, *Defusing the social minefield of gold sites in Kamituga, South Kivu, From legal pluralism to the re-making of institutions ?* **Resources Policy, 53,** 2017, pp. 356-368. https://dx.doi.org/10.1016/j.resourpol.2017.07.009.

[64] S. Geenen, K. Claessens, *Disputed access to the gold mines in Luhwindja, eastern D.R. Congo.* **Journal of Modern African Studies, 51(1),** 2013, pp. 85-108. http://www.jstor.org/stable/43302021.

[65] N. Petrovic, D. Budjelan, S. Cokic, B. Nesi, *The determination of the content of gold and silver in geological sample,* **Journal of the Serbian Chemical Society, 66,** 2001. https://dx.doi.org/10.2298/JSC0101045P.

RETRACTED PAPER on request of the authors regarding intellectual property rights issues.

AN ENVIRONMENTALLY BENIGN APPROACH FOR GOLD RECOVERY FROM GOLD...

[66] M.M. Muanda, P.P.D. Omalanga, *Modeling and Optimization of Manganese Carbonate Precipitation using Response Surface Methodology and Central Compound Rotary Design,* **The Journal of Engineering and Exact Sciences, 7(3),** 2021, pp. 12632–01. https://doi.org/10.18540/jcecvl7iss3pp12632-01-22e.

[67] G.C. Liu, X.L. Wang, *Optimization of critical medium components using response surface methodology for biomass and extra cellular polysaccharide production by Agaricus blazei.*, **Appl Microbiol Biotechnol., 74**, 2007, pp. 78-83. https://doi.org/10.1007/s00253-006-0661-6.

[68] M.S.R.C. Murthy, T. Swaminathan, S.K. Rakshit, Y. Kosugi, *Statistical optimization of lipase catalyzed hydrolysis of methyloleate by response surface methodology,* **Bioprocess Engineering, 22**, 2000, pp. 5–39. https://doi.org/10.1007/PL00009097.

[69] D.X. Wei, S.L. Mao, *Leaching of gold and silver from anode slime with a mixture of hydrochloric acid and oxidizing agents,* **Geosystem Engineering,** 2017. https://dx.doi.org/10.1080/12269328.2017.1278728.

[70] Y.J. Park, D.J. Fray, *Recovery of High Purity Precious Metals from Printed Circuit Boards*, **Journal of Hazardous Materials, 164,** 2009, pp. 1152-1158. http://dx.doi.org/10.1016/j.jhazmat.2008.09.043.

[71] W. Xinchao, C.V. Roger, M.B. Karen, *Recovery of Iron and Aluminum from Acid Mine Drainage by Selective Precipitation,* **Environmental Engineering Science,** 2005, pp. 745-755. http://doi.org/10.1089/ees.2005.22.745.

[72] Z. Liu, M. Frasconi, J. Lei, Z.J. Brown, Z. Zhu, D. Cao, Y.Y. *Botros, Selective Isolation of Gold Facilitated by Second-Sphere Coordination with α-Cyclodextrin,* **Nature Communications, 4,** 2013, pp. 1-9. https://doi.org/10.1038/ncomms2891.

[73] Z. Liu, S.T. Schneebeli, J.F. Stoddart, *Second-Sphere Coordination Revisited*, **Chimia, 68**, 2014, pp. 315-320. https://doi.org/10.2533/chimia.2014.315.