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Characterization and evaluation of glycine and cyanide leaching application on artisanal gold mining tailings

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Abstract: In the artisanal gold mining industry, due to the use of the inefficient amalgamation process, high-grade gold and an alarming quantity of mercury-containing tailings are released to the environment. Although these tailings pose serious environmental risks, they also represent a potentially lucrative source of gold. This study investigates tailings from artisanal gold mining (ASGM) in Cameroon, employing a comprehensive characterization approach that includes physical, chemical, and mineralogical analyses, as well as hydrometallurgical methods such as traditional cyanidation and innovative glycine leaching, complemented by ion exchange to recover metals from the leaching solution. Mineralogical analysis indicated that the sample predominantly consists of quartz and some low-grade silicate and iron minerals. The main constituents were SiO_2, Al_2O_3, and Fe_2O_3. The gold, silver and mercury grades of the sample were 14, 4 and 8 ppm, respectively. The median particle size of the sample (d_{50}) was 360µm. MLA results showed that some of the gold and silver electrums are locked inside quartz, pyrite and muscovite particles. The results of leaching experiments revealed that by applying cyanide leaching, 87% of gold recovery was reached, while the recovery rate of glycine leaching remained around 45%. On the other hand, neither lixiviants did achieve a satisfying mercury recovery, which remained around 30%. The process of grinding the sample resulted in a modest enhancement in the recovery rates of gold and silver; however, it adversely affected the leaching efficiency of mercury during cyanide leaching. The AmberSep M91419 ion exchange resin demonstrated significant efficacy in extracting metals from both cyanide and glycine solutions.

Keywords: ASGM tailings, characterization, gold leaching, mercury removal, glycine leaching

1. Introduction

Artisanal gold mining industry (ASGM) presents an important source of income in developing countries where alternative livelihood sources are limited (Hinton et al., 2003; Fisher, 2007). Despite numerous attempts to give ASGM a precise definition, it seems to vary depending on the region. In some cases, it is considered an illegal mining practice carried out by individuals, families, and cooperative groups using rudimentary tools. In other situations, it is recognized as a fully manual, very small-scale illegal mining activity (Hentschel et al., 2002). In this industry, mercury is used to extract gold and silver from the ground ores through amalgamation. The amalgam is then exposed to a source of heat to evaporate mercury and produce a bullion that consists of gold, silver and other metals (Adams, 2016). But in some cases, mercury is removed by washing with hot nitric acid (Branch, 1994).

The mining industry is notorious for its adverse effect on the environment; however, ASGM, due to the utilization of mercury, plays a bigger role in the phenomenon (Stoffersen et al., 2019). Previous studies made before 2006 have estimated that ASGM releases around 1000 tons of mercury annually (Veiga et al., 2006). According to recent estimations, ASGM stands as the world's largest air and water

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pollutant with mercury, accounting for approximately 37% (2058 tons) of the total mercury emissions annually (Marshall et al., 2020). However, the actual figures surpass these estimations. It was stated that to recover 1 gram of gold, 20 grams of mercury are required. Where 95% of it ends up in the tailings, while the remaining portion is released into the atmosphere (Ilyas and Lee, 2018). According to Youpoungam et al. (2024), this huge amount of mercury released annually serves as a strong indicator that millions of tons of ASGM tailings are generated every year, creating a real threat to the environment.

Despite the aforementioned disadvantages, ASGM has emerged as a significant economic contributor at both the individual and global levels (Marshall et al., 2020). Some reports dated to 1998 estimated that there are more than 55 countries involved in the industries, which suggests that about 100 million citizens depend on this industry to secure their livelihood (Veiga et al., 2006). In Cameroon, for example, ASGM contributes to 20% of the economy (Ralph et al., 2018). In this country, youth represent 80% of the ASGM workers. They earn an average of (156 USD), which is three times the average income of citizens who work in other sectors (Funoh, 2014). Recent reports showed that the ASGM sector expanded to reach more than 70 countries, and it accounts for approximately 20% of the world's total gold production, equivalent to 400 tons of gold per year (Marshall et al., 2020).

According to Youpoungam et al. (2024), ASGM is marked with low gold recoveries. This can be attributed to many factors that affect the amalgamation process, such as gold degree of liberation, gold grain size, pH of the pulp, and mineralogy of the ore, especially sulphide minerals (Marsden and House, 2006). Depending on these factors, in the best conditions, only about 60% of Au can be recovered while the remaining gold reports to the tailing, which makes the ASGM tailing an attractively rich secondary source of gold that draws the attention of small and large mining scale companies (Bansah et al., 2018). The economic potential of the tailings on the other hand, has tempted many researchers to study them in order to propose a possible solution to assess and mitigate their environmental damage, in addition to extracting the precious metals using either well-known methods such as cyanidation or newly invented technologies such as glycine leaching.

For more than a century, cyanide leaching has been the dominant process for extracting gold from primary and secondary sources due to its simplicity and cost-effectiveness. Mining operations worldwide utilize over 18% of the global cyanide production, employing highly water-soluble forms of KCN and NaCN (Birich et al., 2019). The mechanism of gold dissolution in cyanide involves an electrochemical process, where sodium cyanide solutions with low concentrations (100-500 ppm) are used for gold leaching (Syed, 2012). For this electrochemical reaction to take place, oxygen presence is crucial because it helps in the oxidation of gold and therefore the formation of gold-cyanide complex $[Au(CN)_2]^-$. Also, to prevent the formation of volatile hydrogen cyanide (HCN) and reduce the losses of cyanide, the process is normally carried out in a basic environment with a pH of 10.5. However, keeping the pH level above 9.21 is sufficient to prevent HCN formation, which has a pKa of 9.21 at 25 °C (Estay, 2018). Under these conditions, an average dissolution rate of $1.032\ mg.h^{-1}.cm^{-2}$ and an average gold extraction rate of over 90% can be achieved from the free milling gold ores (Birich et al., 2019). In addition to ASGM tailings, gold-bearing ores often contain small amounts of mercury (Sandberg et al., 1984). During the cyanidation process, this co-occurring mercury can be leached along with gold, with extraction rates reaching up to 40% depending on the cyanide concentration and the degree of mercury liberation (Pramudya, 2015). Recently, there has been a growing trend among major mining operators to invest in ASGM by purchasing them and extracting gold through conventional cyanide leaching. However, this practice poses a significant environmental threat as it results in the production of highly toxic cyanide-mercury compounds (Kozin and Hansen, 2013), which can incredibly contaminate inland water through methylation and runoff (Ilyas and Lee, 2018). Additionally, the well-known disadvantages of the cyanidation process have driven the industry to explore alternative methods that can provide safe and ecological gold recovery methods (Hilson and Monhemius, 2006).

Recently, the glycine process was proposed as an alternative to cyanidation. It is a stable and safe amino acid demarcated by two pKa values at 2.34 and 9.6. It has a high solubility in water of around 250 g/l at 25 °C and a melting point of 233 °C. In an alkaline environment, glycine can leach copper, silver, gold, nickel, cobalt, zinc, lead, and some other metal ions due to the presence of carbon and nitrogen atoms (Eksteen et al., 2018). The oxidation potential of amino acids with gold is between 0.55 – 0.8 volts (Adams, 2016), which makes their leaching rate inadequate even at elevated temperatures, necessitating the use of a strong oxidant such as hydrogen peroxide (Eksteen et al., 2018). The newly arising alternative not only resolves the environmental shortcomings but also competes with cyanide in terms of cost and technical efficiency (Oraby et al., 2020) . Using this novel method, Youpoungam et al. (2023) conducted a study to address the environmental concerns associated with the use of cyanide in processing mercury-bearing ASGM tailings. The study concluded that under leaching conditions similar to those of cyanidation, with a pH of 10-11, temperature of 20-25 °C, and glycine and potassium permanganate concentration of 2 g/l, very promising gold and mercury recoveries were achieved within a leaching time of 8 hours. These findings can pave the way for more sustainable exploitation of ASGM tailings and eventually provide a dignified livelihood in the diverse geographies where the industry is practised.

ASGM is mainly practised in Africa, South America and some parts of Asia (Hilson and Maconachie, 2017). This paper is dedicated to studying an ASGM tailings sourced from the Kombo Laka region in Cameroon, which is located approximately 490 km northeast of the capital Yaoundé and 51 km west of the Meiganga district (Ngouo et al., 2021). According to Danga et al. (2023), that region's mineralogical composition mainly consists of quartz, kaolinite and muscovite, in addition to low concentrations of hematite, limonite, gibbsite, orthoclase, albite and calcite. Generally, there are scarce studies on ASGM tailings characterisation (Youpoungam et al., 2024). However, some studies were conducted over samples from this region to serve a diversity of purposes, such as the assessment of soil pollution (Léopold et al., 2016), in addition to the measure of the potentially toxic elements (PTEs) (Danga et al., 2023). This highlights the shortcomings in the characterization of ASGM tailings, rendering the region a highly appealing site for research in this field. Such studies will enhance the understanding of ASGM tailings in the area, paving the way for investments in metal recovery, which could stimulate economic growth and contribute to a cleaner environment. In this study, the targeted sample will be characterized in terms of particle size distribution, mineralogical and chemical properties. In addition, the applicability of gold leaching and mercury removal with the traditional cyanide leaching process as well as the novel and ecofriendly glycine leaching will be tested, also, the suitability of the generated leaching solution to ion exchange resin metals recovery will be investigated which will open the avenue to ecofriendly gold recovery and save mercury removal.

2. Materials and methods

2.1. Materials and reagents

To carry out this study, approximately 13.5 kg of material was collected from the Kombo Laka artisanal mining region in eastern Cameroon, an area characterized by extensive artisanal small-scale gold mining (ASGM) activities. The sample was subjected to riffle splitting to create two equally representative portions. One portion was preserved as a reference sample in a sealed plastic bag, while the other was further divided into sub-samples weighing around 870 grams each, utilizing a rotary sample divider (Fritsch 27), and stored in plastic bags for subsequent experimental studies. For the cyanide leaching process, sodium cyanide (≥ 95%) was used, alongside analytical grade glycine and potassium permanganate for glycine leaching experiments, all procured from Merck. To ensure the pH of the leaching solution remained above 10.5, thereby fostering an alkaline environment and inhibiting the formation of hydrogen cyanide (HCN) during cyanide leaching, sodium hydroxide (99%) and hydrochloric acid (37%) from Isolab were utilized to prepare 2 M pH adjustment solutions. In the adsorption experiments, AmberSep M91419 exchange resin was used. To convert the resin into its chloride form, sodium chloride (>99%), also sourced from Merck, was employed for activation.

2.2. Sample characterization

The particle size distribution of the sample was assessed through vibratory wet sieving, covering a range from 1400 to 38 μm, at the Department of Mining Engineering laboratories at Karadeniz Technical University. To analyze the chemical composition, fire assay and inductively coupled plasma mass spectrometry (ICP-MS) were employed to ascertain the gold grade, while the concentrations of other metals and elements were determined via acidic digestion followed by ICP-MS analysis. Subsequently, X-ray fluorescence (XRF) was utilized to identify the major oxides present in the sample, with all tests being carried out at AR-Ge Test Laboratories in Türkiye. The mineralogical composition was examined using X-ray diffraction (XRD) and scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (EDS) at the Central Laboratories of Karadeniz Technical University. Before analysis, the sample was carbon-coated to ensure an electrically conductive surface. To enhance the understanding of the sample and to gain insights into the liberation of minerals from the gangue, a mineral liberation analysis (MLA) was performed. To improve the analysis results and get more insights into the mineralization, the sample was separated into heavy and light fractions using bromoform (specific gravity = 2.9), from which representative samples were taken. A total of 94 and 27 particles from the heavy and light fractions, respectively, were analyzed using the MLA system in conjunction with scanning electron microscopy (SEM) imaging, with the MLA operating in backscattered electron (BSE) imaging mode. This analysis was conducted at MTA in Türkiye.

2.3. Leaching and metals recovery

The assessment of gold and silver recovery, along with the removal of mercury through hydrometallurgical methods, involved the application of conventional cyanide and oxidative glycine leaching techniques on both the original and ground samples, as well as their respective size fractions. Leaching experiments were conducted on the original and ground samples to observe the leaching behaviour over time, while the leaching of size fractions aimed to evaluate the response of each fraction to the two distinct leaching processes, in addition to quantifying overall metal recovery. This was accomplished by collecting a single sample at the conclusion of each experiment. For the original sample's size fractions, leaching was performed on the fraction ranging from +850 to -75 µm, with nominal fractions of 850, 600, 425, 300, 212, 150, 75, and -75 µm. To investigate the impact of grinding on leaching efficiency, the sample was ground to a size range of +75 to -25 µm, achieving a d_{80} of 74 µm. For this purpose, a laboratory rod mill with a diameter of 19.5 cm was used. The pulp density was 60% solid. The grinding process lasted for 18 minutes at a speed of 42 rpm, which corresponds to 67.7% of the mill's critical speed (62 rpm). After the grinding process, the nominal sizes of the sieves utilized in the screening process included 75, 53, 38, 25, and -25 µm. In the cyanide leaching experiments, the cyanide concentration was set at 1.5 g/l, with a leaching duration of 24 hours. Concurrently, during the glycine leaching experiments, the concentrations of glycine and potassium permanganate were maintained at 3 g/l across the experiment period to provide a sufficient concentration required for the leaching process, with a leaching time of 10 hours. All experiments were conducted at a pH of 10.5, at room temperature, with an agitation speed of 600 rpm, and a liquid-to-solid ratio of 3. Cyanide and glycine leaching conditions were both determined based on the literature. To determine metal concentrations, samples from the leaching solution were analyzed using the Perkin Elmer AAS AAnalyst 400 Atomic Absorption Spectrometer for gold and silver, while mercury concentrations were measured using the same spectrometer in conjunction with the Perkin Elmer/FIAS100 Flow Injection - Atomic Spectroscopy technique. The leaching solution derived from the leaching experiments was employed to evaluate the potential of using ion exchange resin to recover metals. Before conducting the experiments, the adsorbent underwent a thorough washing process with a substantial volume of distilled water to eliminate any residual particles from the fine resin beads that may have been introduced during production or transportation. Subsequently, the resin was subjected to a two-hour washing with six bed volumes of a 2 M sodium chloride solution, which facilitated the complete transformation of the ion exchange active sites to their chloride form. This stage was followed by an extensive washing with water for over two hours to remove any residual sodium chloride from the resin beads. The adsorbent was then dried in a controlled environment at a temperature of 45 °C. After the activation process, specific quantities of the adsorbent were placed into six 100 ml conical flasks, each containing a corresponding volume of solution adjusted to a pH of 10.5, achieving a resin-to-solution ratio of 2. The conical flasks were then positioned in an orbital shaker (Wiggen Hauser) operating at 200 rpm and maintained at 25 °C for a period of 12 hours. During the experiments, samples were collected at intervals of 0.5, 1, 2, 3, 6, and 12 hours, with one flask being removed from the shaker at each sampling time while the others continued to shake, thereby preventing any bias in the results from sampling the same flask multiple times, and the findings were documented accordingly.

3. Results and discussions

3.1. Sieve analysis

Particle size distribution is very crucial in the mining industry; it plays a substantial role in the behaviours of particles during the size reduction operations, concentration and dewatering processes (Fuerstenau and Han, 2003). The result of the particle size distribution of the tailings is presented in Fig. 1. The graph clearly indicates that the sample is relatively coarse, with a median particle size (d_{50}) of approximately 360 µm and d_{80} of 700 µm. This observation strongly implies that the gold present in the tailings is not sufficiently liberated due to the usage of primitive grinding machines in the ASGM sites. This observation is in agreement with what was reported in the literature (De Andrade Lima et al., 2008; Saim et al., 2021). However, the liberation process is more important if gold is to be recovered through the leaching process. According to Veiga and Gunson (2020), the importance of the liberation becomes minimal when applying the gravity concentration process to separate partially liberated gold grains from free quartz particles, where a quartz particle containing 15% gold can acquire a specific gravity of 5.15, which facilitates the separation.

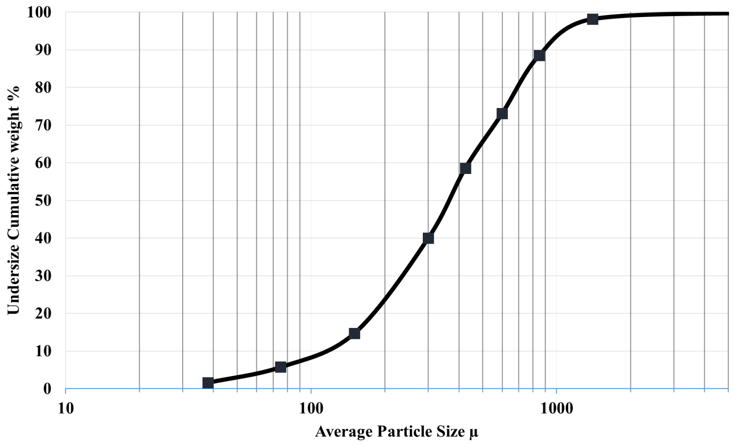

Fig. 1. Particle size distribution of the sample

3.2. Chemical analysis

The results of the chemical analysis are represented in Table. 1. The sample's content of gold was found to be 14.5 ppm while the grades of silver, copper, and mercury were 4.07, 275, and 8.2 ppm, respectively. The high grade of gold can be justified by the tailings' coarse particle size, which led to insufficient liberation of gold and therefore poor recovery of the metal by the amalgamation process. It is well documented that the grain size significantly influences the amalgamation process, as particles smaller than 50µm exhibit poor amalgamation (Marsden & House, 2006). On the other hand, Bansah et al. (2018) reported that ASGM tailings are famous for their high mercury content. According to Veiga et al. (2006) that ASGM tailings generally contain 200 – 250 ppm of mercury coming from the amalgamation process, as is the case in this study. Accordingly, the low content of mercury found in the sample can be due to the large grain size of the sample, which creates channels through which mercury leaks out either because of its high density or the washing out with rainwater or both. However, the sample's mercury content is still alarmingly higher than the globally allowed concentrations, which are determined to be 0.3 ppb Hg in the air for populated areas, 0.001 ppm for drinkable water, and 0.005 ppm for utility facilities (Kozin and Hansen, 2013).

The results of XRF revealed that the main component of the sample was found to be SiO_2, accounting for 78%, accompanied by 9.65% and 5.8% of Al_2O_3 and Fe_2O_3, respectively, as it is revealed in Table. 2. These results align with the results presented by Ayiwouo et al. (2020), who related the abundance of these three oxides to the mineralogical domination of smectite in the area.

Table 1. Concentrations of some important elements in the sample

Element	Au	Ag	As	Hg	Cu	Co	Bi	Ba	La	Mn
ppm	14.45	4.07	4.8	8.2	274.9	45.9	243.1	168.	9.9	724.4
Element	Mo	Ni	Pb	Sb	Sn	Sr	V	W	Zn	Zr
ppm	16.7	16.89	51.9	129.8	<5	4.1	56.6	<5	31	5.4
Element	Al	Ca	Fe	K	Mg	Na	P	S		
%	0.61	0.02	3.12	0.29	0.03	0.01	0.02	0.07		

Table 2. Sample's major oxides composition%

Compound	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	TiO_2	SO_3	P_2O_5	CaO_2	LOI
Grade%	78.07	9.65	5.79	3.38	0.54	0.21	0.17	0.06	0.04	1.94

3.3. Mineralogical analysis

Mineralogically, as it is depicted in Fig. 2, the results of XRD showed a drastic domination of quartz. Kantarcı et al. (2024) reported almost a similar composition of an ASGM sample sourced from Sudan. In addition to quartz, the analysis revealed the presence of various iron minerals such as goethite and iron alpha. Furthermore, the presence of rutile was also identified. For further characterization of the sample, SEM-EDS results were also presented.

The SEM images and EDS spectra are shown in Fig. 3. It can be noticed from the EDS spectrum (a) of spot 1 that gold was found together with some aluminium and iron minerals which indicates that gold was not fully liberated, the percentage of gold in the very spot was found to be more than 93%. The composition of the spectrum (b) of spot 2 was another validation of the domination of quartz in the sample. It also indicates the occurrence of muscovite. Similarly, spectrum (c) shows the composition of spot 2, where the existence of mercury, in addition to some iron and copper was determined. The existence of sulphur at this spot not only indicates the presence of some iron and copper sulphide minerals but might also indicate that the sample contains some mercury sulphide, which has a very low solubility (Dyrssen and Wedborg, 1991), which explains the low recovery of mercury during leaching experiments. According to Marsden and House (2006), the existence of sulphide minerals and sulphur leads to the formation of highly insoluble HgS according to Equation 1.

$$\mathrm{Hg}^{2+} + \mathrm{S}^{2-} \rightleftharpoons \mathrm{HgS} + \mathrm{Hg}^{o} \tag{1}$$

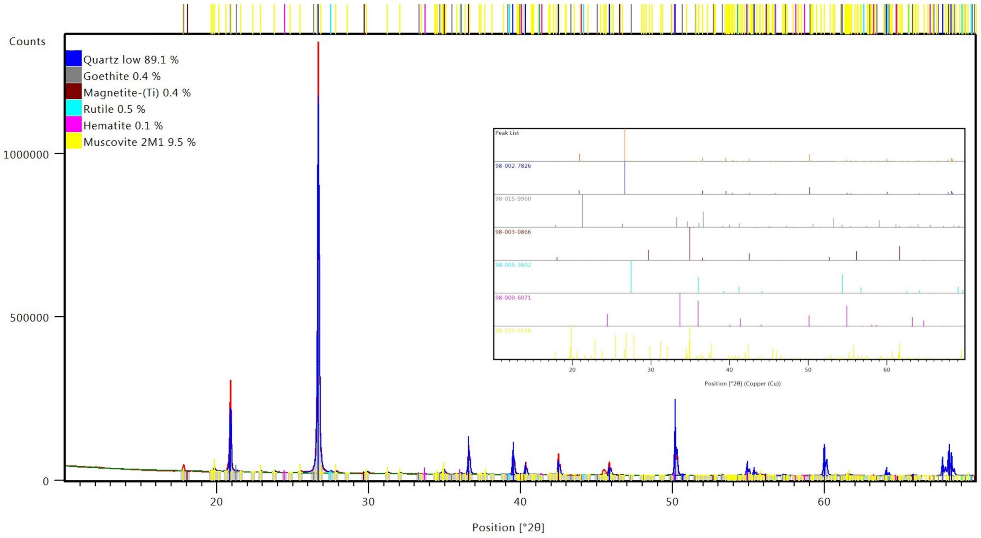

Fig. 2. XRD Rietvelt analysis of the sample

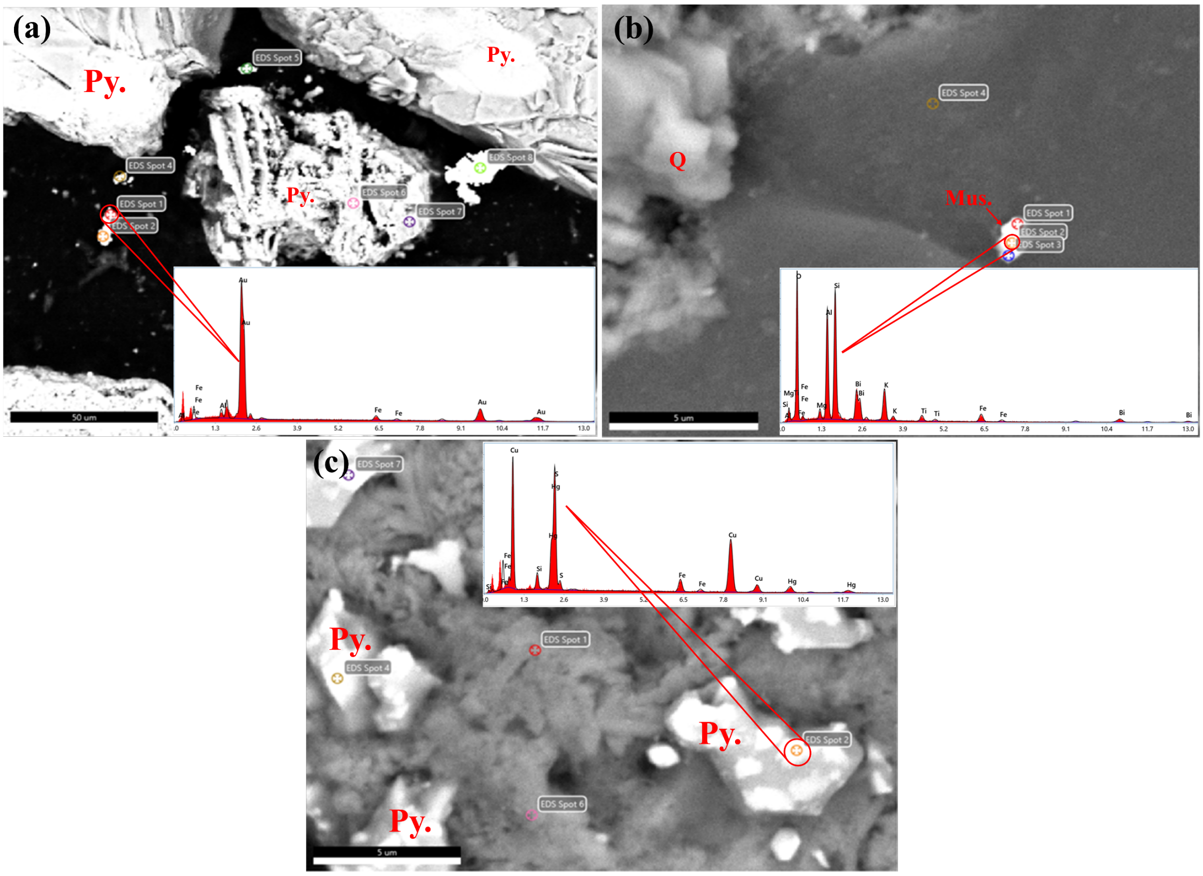

Fig. 3. SEM Imaging and EDS spectra of the sample

3.3.1. Mineral liberation analysis

MLA provides significant support in evaluating the grade of associated minerals, which is crucial for enhancing the mineral beneficiation process (Sandmann, 2013). Furthermore, it serves as a tool for evaluating the liberation of valuable minerals from gangue materials. The objective of the MLA analysis in this particular study is to further identify the grades of the associated minerals rather than assessing the degree of targeted minerals liberation. The findings from the MLA analysis conducted in this research are illustrated in Fig. 4. In Fig. 4 (a), it is evident that the light fraction of the sample is predominantly composed of quartz and muscovite, accounting for 70% and 25%, respectively. The coloured map indicates that some gold and silver electrum (represented by yellow spots) are encapsulated within quartz particles, while a portion of the electrum is partially liberated and located at the edges of these quartz particles. This observation is due to the large particle size of the sample discussed in section (3.1). Conversely, the MLA analysis results for the heavy fraction of the sample are depicted in Figs. 4 (b), (c), and (d). Similar to the light fraction, where quartz was the primary mineral, the heavy fraction is largely comprised of iron oxide along with a variety of other minerals, including pyrite and muscovite. The presence of iron oxide in the sample is believed to have resulted from the long-term alteration of pyrite. It is observed in Figs. 4 (b) and (c) that electrum is trapped within pyrite and muscovite. Additionally, the analysis revealed the presence of silver sulphide mineral (acanthite) as a locked particle within the iron oxide, as shown in Fig. 4 (d).

The chemical and mineralogical analysis reveals that a portion of the targeted metals, particularly gold and silver, is encapsulated within quartz and pyrite minerals. This encapsulation hinders their liberation, thereby preventing effective extraction through amalgamation. Furthermore, it suggests that additional grinding is necessary to enhance the degree of liberation, which would improve the recovery rates of gold and silver. Additionally, it suggests that the presence of pyrite can lead to the formation of sulfide ions in solution, which subsequently results in the passivation of gold dissolution and an increase in cyanide consumption (Dai and Jeffrey, 2006).

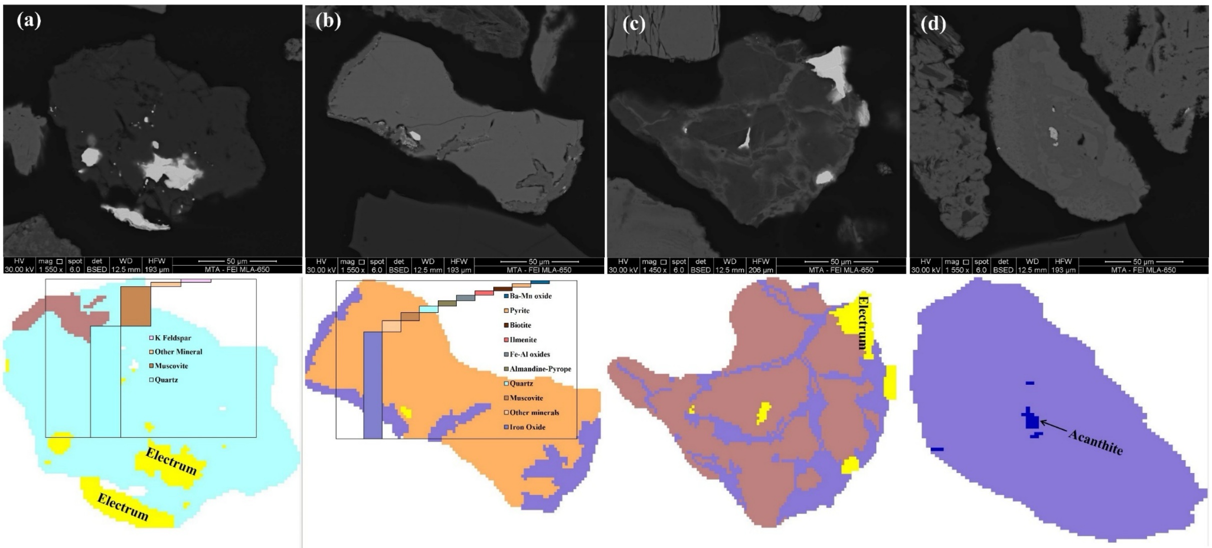

Fig. 4. SEM-BSE and classified MLA image of the light fraction (a), and heavy fraction different particles (b), (c) and (d)

3.4. Leaching results

In this study, both cyanide and glycine leaching were tested on the sample. As it is depicted in Fig. 5. (a), the cyanide leaching process yielded a gold recovery of 87% over a 24-hour period, while only 28% of the mercury was extracted. Conversely, silver recovery was notably higher, reaching 78.2% by the conclusion of the experiment. These results show similarities with those reported in the literature. Alkloos and Aydoğan (2024) have conducted research on a mineralogically similar ASGM sample. They found that under experimental conditions of stirring speed of 400 rpm, a temperature of 25 °C, a liquid/solid ratio of 1.5, a pH of around 10.5 and a cyanide concentration of 500 ppm, 87.5% can be achieved. In another study done by Pramudya (2015) It was reported that the extraction rates of mercury alongside gold can vary between 10% – 40%, depending on many factors such as cyanide concentration and the degree of mercury liberation. On the other hand, De Andrade Lima et al. (2008) claimed that they were able to achieve gold and mercury recoveries of 89% and 100%, respectively. However, the findings reported in the later study are questionable due to the insufficient information provided about the leaching process conditions.

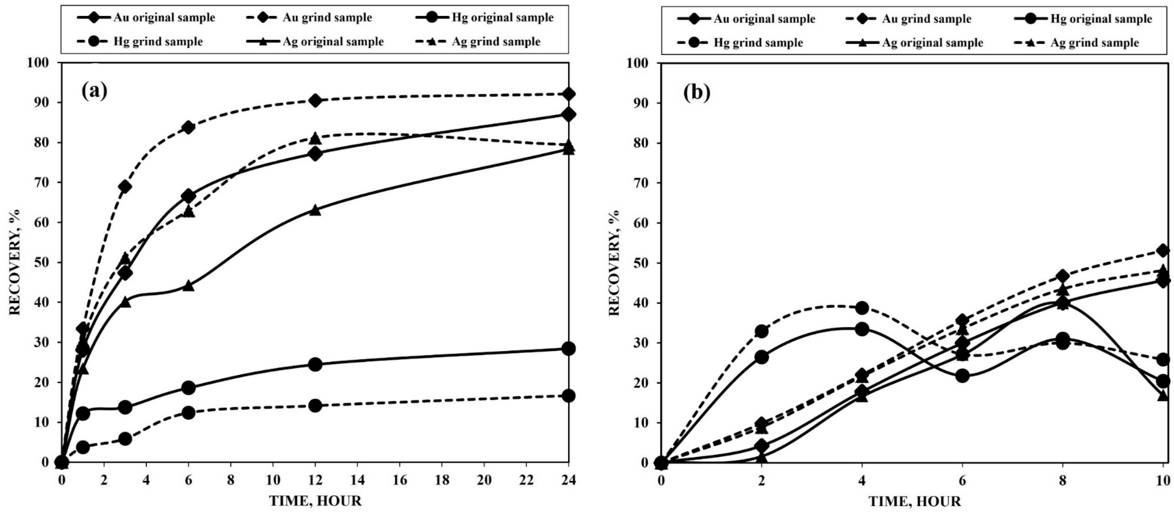

Fig. 5. Results of the original sample and grind sample cyanide leaching (a), pH 10.5, NaCN 1.5 g/l, L/S 3 and agitation speed 600 rpm at room temperature. Glycine leaching (b), pH 10.5, glycine 3 g/l, potassium permanganate 3 g/l, L/S 3 and agitation speed 600 rpm at room temperature

In a study conducted by Youpoungam (2023), under leaching conditions of pH range of 10-11, a temperature of 20-25 °C, and a glycine concentration of 2 g/l, more than 90% of the gold and mercury were recovered from a fine grinding ASGM tailings within 8 hours. In light of these findings, the leaching experiments of gold and mercury were conducted for a period of 10 hours, as shown in Fig. 5 (b). It can be seen that all metal recoveries were very low. Where only 45.6% of the gold was extracted. Mercury recovery reached its peak of 33% at the 4th hour, followed by a subsequent fluctuation between 20% and 30% up until the end of the experiment. Silver recovery was similarly low, where it reached its maximum of 40% at the 8th hour before declining to approximately 20% by the end of the experiment.

The observed low rates of gold extraction during both cyanide and glycine leaching processes can be attributed to the entrapment of certain gold grains within the coarse particles of the sample. While recovery of gold with cyanide from the grind sample reached up to 68% after two hours, its equivalent recovery from the coarse sample remained around 46%. This entrapment necessitates an extended duration for cyanide to diffuse into the occluded gold particles, while glycine, due to its larger molecular size, requires an even longer time to access the unliberated particles and achieve a recovery closer to that of cyanide. The rate of gold leaching in a solution with 0.5 M glycine and 1% hydrogen peroxide at a pH of 11 after 48 hours was measured at 0.322 $\mu mol/m^2.s$, which is lower than the leaching rates observed with cyanide (Oraby and Eksteen, 2015). Furthermore, existing literature suggests that the glycine leaching process in this investigation was not given adequate time in comparison to the cyanide leaching process. Comparing gold recoveries at the 6th hour for both cyanide and glycine, it can be seen that when the cyanide leaching rates reached 68% and 84% for coarse and ground samples, glycine leaching rates remained at 29% and 36%, respectively. In a related context, the inadequate recovery of mercury may stem from intense competition between mercury and silver during the leaching operations, coupled with the potential presence of mercury in the form of cinnabar, which is notoriously challenging to leach.

To assess the impact of grinding on the leaching process, the sample was processed to a particle size of -106 µm. As illustrated in Fig. 5, there was a general enhancement in leaching rates. Specifically, as shown in Fig. 5 (a), the overall recovery of gold improved, with 93% of gold being extracted from the ground sample, reflecting a 6% increase. However, an intriguing observation was made regarding mercury leaching, where grinding the sample adversely affected the recovery, leading to a decrease from 28% in the original sample to 16% in the ground sample. Conversely, despite the increased leaching rates, the overall recovery of silver remained unchanged. In the context of glycine leaching, as depicted in Fig. 5 (b), grinding the sample resulted in a modest 4% increase in overall gold recovery. Additionally, although there was a slight improvement in mercury recovery, its rates were not stable over time. Along with the presumable presence of cinnabar, the low mercury recovery can be attributed to the formation of mercury sulphide, difficult to dissolve, as a result of contact between mercury used in amalgamation and the sulphur found in pyrite. During the grinding process, mercury used in the amalgamation process comes in contact with some liberated pyrite particles. Then, as a result of the high affinity of mercury to sulphur, a chemical reaction takes place between mercury and pyrite, leading to the formation of mercury sulphide, as shown in Equation 1. In contrast, silver recovery exhibited a significant enhancement, with an 8% increase compared to the highest recovery achieved during the original sample leaching. The relatively low recovery of metals during glycine leaching can be explained by the prolonged duration required for amino acid leaching processes to yield satisfactory metal recovery, as noted by Eksteen and Oraby (2015), although conflicting findings have also been reported. These discrepancies can be attributed to the characteristics of the ore and the oxidants employed during the leaching process. Potassium permanganate and hydrogen peroxide are the most used oxidants in the glycine leaching process however, they possess different reduction potentials, with peroxide being superior. Equations 2. and 3. (Altinkaya et al., 2020; Oraby et al., 2020) demonstrate the complexation reaction of gold with glycine in the presence of hydrogen peroxide and permanganate, respectively.

$$2Au + 4NH_2CH_2COOH + 2OH^- + H_2O_2 \rightarrow 2Au(NH_2CH_2COO)_2 + 4H_2O \tag{2}$$

$$\begin{gathered} Au + 2MnO_4^- + 4(NH_2CH_2COO)^- + O_2 \rightarrow Au(NH_2CH_2COO)_2 + \\ +2MnO_2 \downarrow +2C_2O_4^{-2} + 2NH_{3(aq)} + 2OH^- \end{gathered} \tag{3}$$

The findings from the original sample size fractions concerning cyanide and glycine leaching are illustrated in Figs. 6 (a) and (b). During the cyanide leaching process, it was observed that the recoveries of gold, mercury, and silver improved as the particle size of the sample decreased from +850 to +450 µm, achieving recoveries of 85%, 20%, and 78%, respectively. Beyond this point, gold recoveries remained relatively stable, with the exception of the -75 µm size fraction, which yielded the highest recovery of 90%. Conversely, mercury recovery experienced a significant decline as the particle size gets finer, remaining between 5% and 10% for the remaining fractions. A similar pattern was evident in silver recovery, which fluctuated between 40% and 70%. Notably, selective leaching was effective for the -75 µm size fraction, resulting in recoveries of 90.7% for gold, 72% for silver, and 8.7% for mercury. In the case of glycine leaching, a trend of increasing metal recoveries was observed as the sample size decreased from +850 to +600 µm, achieving peak recoveries of 61%, 58.5%, and 57% for gold, silver, and mercury, respectively. However, recoveries for gold and mercury declined in the subsequent fractions of +425 and +300 µm, with mercury continuing to decrease in the +212 µm fraction. Following this, gold recovery gradually increased across the subsequent size fractions, reaching 60% at +75 µm before slightly dropping to 51% at -75 µm. Mercury exhibited a similar trend after the +212 µm fraction. Silver initially mirrored the behaviour of gold and mercury in the earlier size fractions, peaking at +600 µm, then declining to approximately 30% before remaining relatively constant in the following fractions, with a subsequent increase at the +75 µm fraction.

Gold and silver recoveries are generally more effective with cyanide leaching compared to glycine leaching across various size fractions. However, glycine leaching demonstrates a superior capacity for mercury extraction when juxtaposed with cyanide. This superior performance can be attributed to the slower diffusion rate of glycine into the ore particles, allowing for increased interaction between glycine and mercury, thereby improving mercury leaching outcomes. This observation aligns with the findings of Youpoungam (2023), who reported exceptionally high recoveries of gold and mercury exceeding 90% from a sample sourced from Sudan using glycine. This stark contrast in leaching efficacy can be linked to the traditional artisanal grinding techniques employed. In Sudan, ASGM ores referenced in the study above are processed using wet wheeled grinding mills, which perform size reduction by pressing the ore against the mill walls by means of their rotating wheels, akin to the mechanisms of vertical roller mills (VRM). This method generates fractures that facilitate the penetration of the leaching solution into the particles. In contrast, the sample used in the current study was ground using a dry hammer mill, which operates by striking the ore with high-speed rotating hammers, in a manner similar to that of hammer crushers. This technique tends to leave the particles unfractured and unstressed, resulting in more challenging diffusion of the leaching solution.

The evaluation of the leaching performance across various size fractions of the grind sample was conducted, with the findings illustrated in Fig. 7. In the context of cyanide leaching, as depicted in Fig. 7 (a), all size fractions exhibited commendable gold recovery rates exceeding 90% which considered to be within the range of gold recoveries achieved in the industrial scale of the free milling ores processing

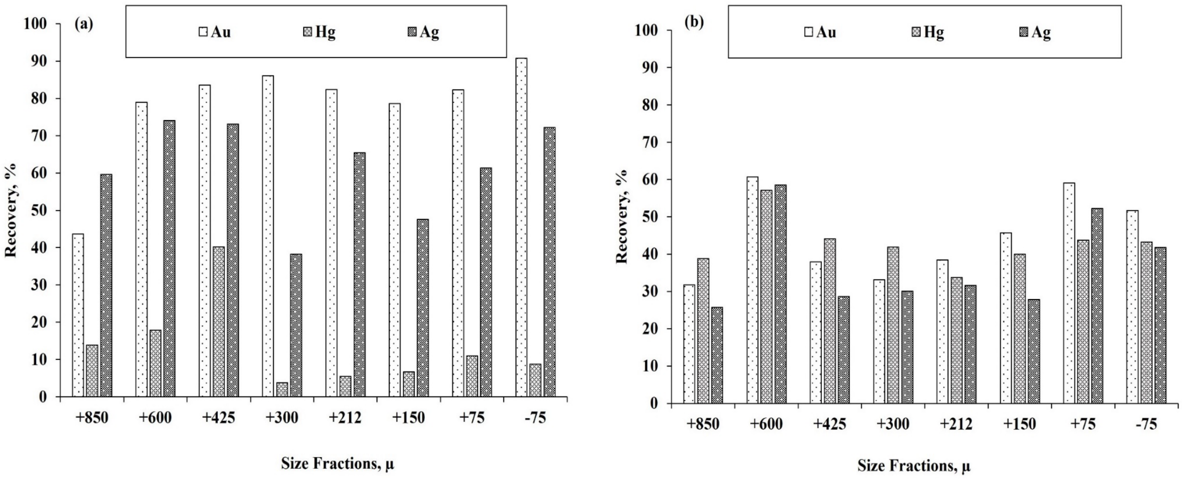

Fig. 6. Results of the original sample's size fractions cyanide leaching (a), pH 10.5, NaCN 1.5 g/l, time 24 hours, L/S 3 and agitation speed 600 rpm at room temperature. Glycine leaching (b), pH 10.5, glycine 3 g/l, potassium permanganate 3 g/l, time of 10 hours, L/S 3 and agitation speed 600 rpm at room temperature

(Marsden and House, 2006). On the other hand, silver recovery rates remained in the range between 70% and 83%. Conversely, the leaching of mercury did not exhibit any notable enhancement, but in some cases was worse than that of the original sample. Notably, the fraction measuring less than 25 µm achieved the highest gold recovery rate of 97%, alongside satisfactory silver recovery, indicating that finer grinding is essential for maximizing gold liberation. In terms of glycine leaching, as shown in Fig. 7 (b), the performance across size fractions did not yield a significant improvement in the overall metals leaching. Furthermore, there was an absence of a discernible trend in the leaching behaviour of metals, contrasting with the more predictable patterns observed during cyanide leaching. This suggests that, in addition to the inherent complexities of the ore, further investigations are required to optimize metal recovery.

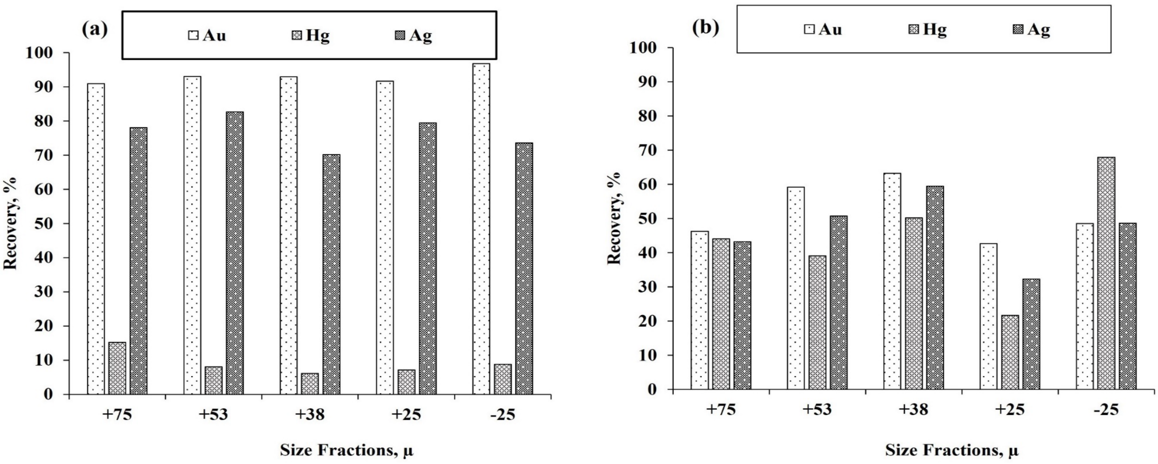

Fig. 7. Results of the grind sample's size fractions cyanide leaching (a), pH 10.5, NaCN 1.5 g/l, time 24 hours, L/S 3 and agitation speed 600 rpm at room temperature. Glycine leaching (b), pH 10.5, glycine 3 g/l, potassium permanganate 3 g/l, time of 10 hours, L/S 3 and agitation speed 600 rpm at room temperature.

3.5. Metals recovery from solution

Activated carbon remains the predominant adsorbent utilized in the field of gold hydrometallurgy; however, contemporary ion exchange resins present numerous advantages that may surpass those of activated carbon. A notable benefit is the straightforward nature of the elution process associated with ion exchange resins, which does not necessitate elevated temperatures (Harris et al., 1992; Xu et al., 2017). Furthermore, these resins demonstrate a high degree of selectivity for organic complexes, with gold-selective resins proving particularly effective in recovering gold from preg-robbing scenarios and in managing elevated concentrations of base metals in pregnant leach solutions (Xu et al., 2017). The resin employed in this investigation, AmberSep 91419 (MINIX), has received commendation from the Anglo Asian Mining company for its efficacy in extracting gold from cyanide pregnant leach solutions (PLS) containing approximately 1-2 ppm of gold, alongside significant copper levels exceeding 1000 ppm. The outcomes of utilizing this resin in both cyanide and glycine solutions are illustrated in Fig. (8) (a) and (b), respectively. The data indicate that metal recovery rates surpassed 95% for both solutions, with the exception of mercury recovery from the glycine leaching solution, which remained around 85%. This lower recovery rate for mercury can be attributed to the higher concentration of glycine present in the leaching solution compared to the cyanide used in the cyanide leaching process, which may result in a competitive behaviour during the adsorption process. On the other hand, it can be seen that gold and mercury adsorption rates from cyanide solution are superior to those from glycine. While metals uptake of gold, mercury and silver from cyanide solution reached 100%, 96.6%, and 95.7%, those from glycine solution were found to be 96.8.2%, 84.4%, and 100%, respectively. The findings presented are confirmed by existing literature in the field. A notable investigation by Staker and Sandberg (1987) detailed the application of various ion exchange resins, such as lRA-430, 900, 2lK, SMA-I, and SBR, for the selective extraction of gold, silver, and mercury from cyanide PLS. These resins demonstrated significant efficacy in eliminating mercury-cyanide complexes from the aqueous phase. Furthermore, a contemporary study by Deng et al. (2020) introduced a novel resin, IXOSAuC, which, under experimental conditions of pH 10.5 and an adsorbent dosage of 6 g/l, achieved a remarkable 100% recovery of gold.

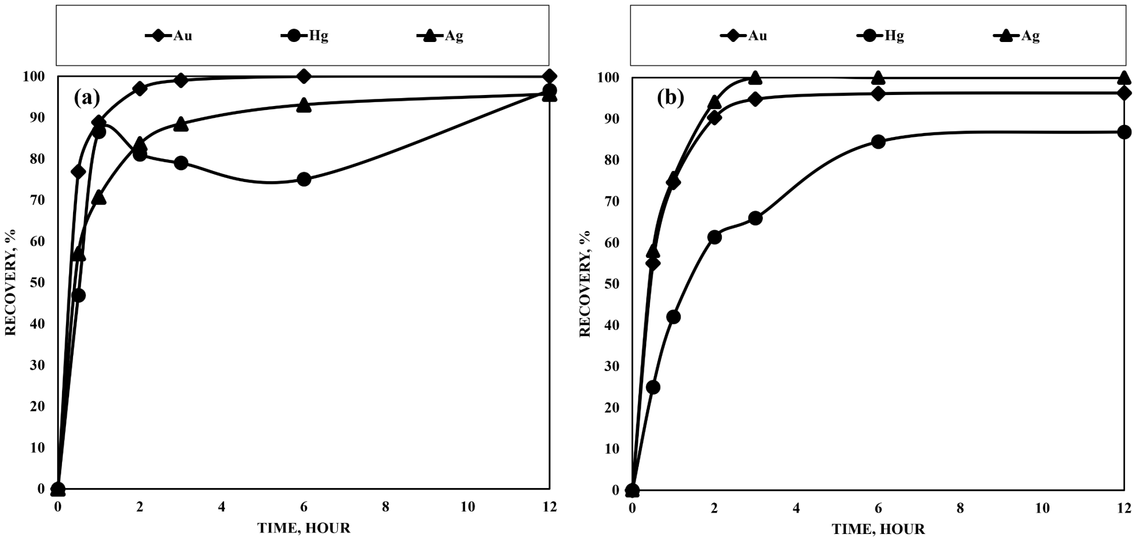

Fig. (8). Metals recovery from cyanide (a) and glycine (b) leaching solutions using AmberSep 91419 ion exchange resin, pH 10.5, 12 hours, resin/solution 2 g/l, agitation speed 200 rpm at room temperature

4. Conclusions

This research primarily focused on characterizing the sample and evaluating the feasibility of utilizing cyanide and glycine leaching methods for the economic and environmentally friendly extraction of Au, Ag and Hg from tailings. The characterization results indicated that the sample was predominantly composed of quartz. Chemical analyses revealed that mercury content was found to be 8 ppm, posing a considerable ecological threat, and that the sample content of gold was 14.45 ppm, most of which, according to Mineral Liberation Analysis (MLA), are encapsulated within quartz, muscovite, and certain iron minerals. During leaching evaluation tests, cyanidation resulted in a commendable gold recovery rate of 87%. In contrast, glycine leaching only attained a recovery of 45%, which was attributed to the large particle size of the sample (d_{80} = 700 μm). The mercury leaching rates were notably low, likely due to competition created by other metals or the presence of mercury in the form of stable mercury sulfide, resulting from interactions between mercury used in the amalgamation and sulfur in pyrite. Although grinding the sample led to improvement in gold and mercury recovery, especially during glycine leaching, it negatively impacted mercury leaching efficiency during the cyanidation process. The lower silver recovery compared to gold can be explained by the mineralization of silver as acanthite, which is challenging to dissolve. Using AmberSep M91419 ion exchange resin, more than 95% of gold, mercury and silver were recovered from both leaching solutions within 12 hours, however, mercury recovery from the glycine solution remained within the range of 85%.

Overall, while cyanide can yield favourable results, its use on mercury-laden resources is restricted by the Minamata Convention, thus emphasizing the importance of advancing glycine leaching as a viable alternative that could benefit both economic and environmental objectives. The authors believe that if the sample is sufficiently ground and the leaching time is extended, the gold and mercury leaching rate of glycine can be tremendously enhanced, hence safer gold recovery and mercury removal can be possible. Additionally, the authors think that more characterization is required to identify the nature of mercury in the sample, according to which suitable removal and mitigation procedures can be made in case glycine leaching does not achieve the expected results.

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