

KARADENİZ TECHNICAL UNIVERSITY
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

DEPARTMENT OF MINING ENGINEERING

**THE SELECTIVE RECOVERY OF GOLD AND MERCURY FROM
AMINO ACID LEACHING LIQUOR**

MASTER THESIS

Abdulbagi Hassan Abdallah MOHAMED

JANUARY 2024

TRABZON



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**This thesis is accepted to give the degree of
"MASTER OF SCIENCE"**

**By The Graduate School of Natural and Applied Sciences at
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Supervisor : Prof. Dr. İbrahim ALP

Trabzon 2024

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To convey this sentiment, I turn to the words of George Shinn, who said, "No one achieves success alone. It is only with the help of others that we can reach our goals." Recognizing the significant contributions of certain individuals is essential in fully acknowledging the accomplishment of this work.

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Abdulbagi Hassan Abdallah MOHAMED

Trabzon 2024

DECLARATION

I, the signatory, hereby affirm that this thesis entitled (The Selective Recovery of Gold and Mercury from Amino Acid Leaching Liquor) embodies the results of my own handwork, meticulously conducted fully under the supervision of Prof. Dr. İbrahim ALP, subsequent to my enrolment in the prestigious Karadeniz Technical University for the pursuit of a master's degree. Also, all parts in this thesis which are not my own work have been identified. Furthermore, I confirm that this thesis has not been previously submitted, either in its entirety or partially, for any degree or qualification at this or any other institution. 25.01.2024.

Abdulbagi Hassan Abdallah MOHAMED

LIST OF CONTENT

	<u>Page No</u>
ACKNOWLEDGEMENTS	III
DECLARATION.....	IV
LIST OF CONTENT	V
SUMMARY	III
ÖZET	IV
LIST OF FIGURES	V
LIST OF TABLES	VIII
LIST OF SYMBOLS AND ABBREVIATIONS	X
1. INTRODUCTION	1
1.1. Overview	1
1.2. Problem Statement	2
1.3. Aims and Objectives	3
2. LITERATURE REVIEW	5
2.1. Introduction	5
2.2. Gold Characteristics	5
2.3. Gold Mining Industry	6
2.4. Gold Amalgamation	7
2.5. Artisanal Gold Mining Industry	10
2.5.1. Harmful Effects of Mercury	12
2.6. Gold Leaching Process	14
2.6.1. Cyanide Leaching	15
2.6.2. Gold Leaching with Amino Acids	18
2.6.3. Glycine Leaching	18
2.7. Recovery of Gold and Mercury from PLS	22
2.7.1. Activate Carbon Adsorption	22
2.7.2. Ion Exchange Resin Adsorption	25
2.7.3. AmberSep 91419 Resin (MINIX)	29
2.7.4. Purolite A500Cplus Resin.....	31
2.7.5. Adsorption Kinetics Models	31
2.7.6. Adsorption Isotherms	33

2.8.	Gold and Mercury Elution.....	35
2.9.	Activated Carbon Elution Methods	35
2.9.1.	Zadra Elution Process	37
2.9.2.	Anglo American Research Laboratories (AARL) Elution Process	38
2.9.3.	Organic Solvent-Assisted Elution	38
2.10.	Ion Exchange Resin Elution Methods	39
2.10.1.	Elution of Strong-Base Resins	39
2.10.2.	Elution of Weak-Base Resin	43
2.11.	Justifications of the Thesis	45
3.	MATERIAL AND METHODS	47
3.1.	Introduction	47
3.2.	Materials	47
3.2.1.	Chemical Materials	47
3.2.2.	Adsorbents Used in the Thesis.....	49
3.2.3.	Instruments.....	51
3.3.	Sample Preparation.....	52
3.4.	Sample Characterization.....	52
3.5.	Methods.....	54
3.5.1.	Adsorbents Pretreatment	54
3.5.2.	Original Solution Preparation	55
3.5.3.	Synthetic Solution Preparation.....	56
3.5.4.	Resins Screening Test	57
3.5.5.	Adsorption Process Optimization	59
3.5.6.	Adsorption Kinetics Test	60
3.5.7.	Adsorption Isotherms	61
3.5.8.	Mercury Elution Preliminary Tests.....	61
3.5.9.	Mercury Elution Experiment	62
3.5.10.	Gold Elution Preliminary Tests.....	62
3.5.11.	Gold Elution Experiments.....	63
3.5.12.	Elution Kinetics.....	64
3.6.	Cycle Test.....	64
3.7.	Analysis and Characterization.....	65
3.7.1.	Analysis Method	65
3.7.2.	Adsorbents Characterization	67

4. RESULTS AND DISCUSSIONS.....	68
4.1. Resins Screening Test	68
4.2. Adsorption Experiments Results	69
4.2.1. Effect of Temperature	71
4.2.2. Effect of pH.....	73
4.2.3. Effect of Adsorbent Dosage	76
4.2.4. Effect of Retention Time.....	78
4.2.5. Effect of Shaking Speed.....	79
4.2.6. Adsorption Kinetic Models	82
4.2.7. Adsorption Isotherms	93
4.3. Elution Experiments Results	94
4.3.1. Mercury Elution Pre-Tests	95
4.4. Effect of Parameters on Mercury Elution.....	97
4.4.1. Effect of Eluent Concentration	97
4.4.2. Effect of Bed Volume	98
4.4.3. Effect of Retention Time.....	99
4.4.4. Effect of Temperature	100
4.4.5. Kinetics of Mercury Elution	101
4.5. Gold Elution Pre-Tests	102
4.6. Parameters Effect on Gold Elution.....	104
4.6.1. Effect of Sodium Chloride Concentration	104
4.6.2. Effect of Sodium Hypochlorite Concentration	105
4.6.3. Effect of Eluent Bed Volume.....	107
4.6.4. Effect of Retention Time	108
4.6.5. Effect of Temperature	110
4.6.6. Gold Elution Kinetics.....	111
4.6.7. Cycle Test	112
4.6.8. Adsorbents Characterization	116
5. CONCLUSION.....	123
6. PROPOSED FURTHER WORK.....	125
7. REFERENCES	126
BIOGRAPHY	

Master's Thesis

SUMMARY

THE SELECTIVE RECOVERY OF GOLD AND MERCURY FROM AMINO ACID LEACHING LIQUOR

Abdulbagi Hassan Abdallah MOHAMED

Karadeniz Technical University

The Graduate School of Natural and Applied Sciences

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Supervisor: Prof. Dr. İbrahim ALP

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This study aimed to examine the adsorption and selective elution of Au and Hg from glycine pregnant solution using Purolite 500Cplus and AmberSep 91419 IX resins and activated carbon. The impact of temperature, pH, amount of adsorbent, duration of retention, and speed of shaking on adsorption were considered. The results showed that temperature and pH compared to others had minimal effects on Au adsorption, but together with adsorbent dosage played a significant role in Hg adsorption. Under optimal conditions, ~100% of Au and Hg were adsorbed onto IX resins, with Hg adsorption onto AC remained around 80%. The PSO model was the best to describe the adsorption kinetics. Au adsorption onto IX resins fit better with the FAIM and its adsorption onto AC with the LAIM model. Regarding the selective elution process, H₂SO₄ and a mixture of NaOCl, NaCl, and NaOH were chosen for Hg and Au elution, respectively. The impact of four different factors, namely eluent concentration, bed volume, elution time, and temperature, on Hg and Au elution was investigated. Under ideal conditions, 100% of Hg and ~1% of Au were eluted during mercury elution stage. For Au elution, temperature, eluent volume, and NaOCl concentration were identified as the most influential parameters. At the optimum conditions, all Au and approximately 60% of Ag were eluted. Cycle tests indicated that Purolite was easier to elute, and regenerate compared to AmberSep, although it was less durable.

Keywords: Adsorption, Elution, Gold, Mercury, Glycine Leaching, ASGM, IX Resin.

ÖZET

AMİNO ASİT LİÇ ÇÖZELTİSİNDEN ALTIN VE CİVA'NIN SEÇİCİ GERİ KAZANIMI

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Bu çalışma, Purolite, AmberSep IX reçineleri ve aktif karbon kullanarak Au ve Hg'nin glisin çözeltisinden adsorpsiyonunu ve seçici sıyırılmasını incelemeyi amaçlamıştır. Sıcaklık, pH, soğurucu miktarı, alıkonma süresi ve çalkalama hızının adsorpsiyon üzerindeki etkisi değerlendirilmiştir. Sonuçlar, sıcaklık ve pH'ın diğerlerine kıyasla Au adsorpsiyonu üzerinde minimum etkiye sahip olduğunu, ancak adsorban dozajı ile birlikte Hg adsorpsiyonunda önemli bir rol oynadığını göstermiştir. Optimum koşullar altında, Au ve Hg'nin ~%100'ü IX reçinelerin yüzeyine soğurulurken, Hg'nin %80'i AC üzerine soğurulmuştur. Adsorpsiyon kinetiğini tanımlamak için PSO, en uygun model olmuştur. IX reçineleri üzerine Au adsorpsiyonu FAİM ile, AC üzerine adsorpsiyonu ise LAİM ile daha iyi uyum göstermiştir. Hg ve Au'yu seçici olarak sıyırmak için, H₂SO₄ ve % 0,75 v/v NaOCl, 150g/l NaCl ve 5g/l NaOH karışımı sırasıyla Hg ve Au sıyırmak için en uygun sıyırıcı olarak seçilmiştir. Sıyırıcı konsantrasyonu, sıyırıcı miktarı, temas süresi ve sıcaklık dört farklı faktörün Hg ve Au sıyırması üzerindeki etkisi araştırılmıştır. Hg sıyırma aşamasında, ideal koşullar altında, Hg'nin %100'ü ve Au'nun ~%1'i sıyırılmıştır. Au sıyırması için, sıcaklık, sıyırıcı miktarı ve NaOCl konsantrasyonu en etkili parametreler olarak belirlenmiştir. Optimum koşullarda, Au'nun tamamı ve Ag'nin yaklaşık %60'ı sıyırılmıştır. Tekrar testleri, Purolite'in AmberSep'a kıyasla daha az dayanıklı olmasına rağmen sıyırma ve yeniden oluşumunun daha kolay olduğunu göstermiştir.

Anahtar Kelimeler: Adsorpsiyon, Sıyırma, Altın, Cıva, Glisin Liçi, ASGM, IX Reçinesi.

LIST OF FIGURES

	<u>Page No</u>
Figure 1. Gold and silver amalgamation (Marsden & House, 2006).....	8
Figure 2. Gold prices in the last four decades in USD/Oz (URL-2, 2023).....	11
Figure 3. Accumulation of mercury in human's body (Subeshan et al., 2023).	14
Figure 4. Speciation of cyanide and hydrogen cyanide in aqueous solution as a function of pH (Marsden and House, 2006).	16
Figure 5. Optimized geometries of Au- Glycine complexes (Xie, et al., 2012).	19
Figure 6. Eh-pH diagram showing typical operating regions for gold lixivants (Adams, 2016).	20
Figure 7. Effect of temperature (a), and pH (b) on aurocyanide adsorption onto AC (Marsden & House, 2006).....	23
Figure 8. Equilibrium loading of various metal cyanide complexes (a) and the effect of pH on base metals loading onto strong base resin (b) (Marsden & House, 2006)	26
Figure 9. Effect of temperature (a), organic solvent addition (b), and the eluant flow rate (BV/hr) on the elution of aurocyanide from AC (Marsden and House, 2006).....	36
Figure 10. Elution rate of gold from a strong base resin using different eluents (Marsden & House, 2006)	41
Figure 11. Difference in the elution rates between strong base and weak base resins (Marsden & House, 2006).	44
Figure 12. Particle size distribution of the sample	52
Figure 13. XRD profile of the ASGM tailings sample	53
Figure 14. IX resins upon introducing to the screening test.	57
Figure 15. Gold elution experiments steps, placing resin to the tube (a), solution addition (b) placing the tube into orbital shaker (c).	64
Figure 16. Hg Calibration curve of FIAS 100	66
Figure 17. Surface Plot of Au adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of temperature °C and adsorbent dosage (g/l).	71
Figure 18. Surface Plot of Hg adsorption onto Purolite A500 CPlus (a), AmberSep M91419 (b) and AC (c). As function of temperature °C and adsorbent dosage (g/l).	72
Figure 19. Surface Plot of Au adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of pH and adsorbent dosage (g/l).	73

Figure 20. Surface Plot of Hg adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As a function of pH and adsorbent dosage (g/l).	75
Figure 21. Surface Plot of Au adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of adsorbent dosage (g/l) and shaking speed (rpm).	77
Figure 22. Surface Plot of Hg adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of adsorbent dosage (g/l) and shaking speed (rpm).	77
Figure 23. Surface Plot of Au adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of adsorbent dosage (g/l) and, contact time (hr).	78
Figure 24. Surface Plot of Hg adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of adsorbent dosage (g/l) and contact time (hr).	79
Figure 25. Surface Plot of Au adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of shaking speed (rpm) and, Contact time (hr).	80
Figure 26. Surface Plot of Hg adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of shaking speed (rpm) and, Contact time (hr).	81
Figure 27. Fitting the data of Au adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c) to IPD model.	91
Figure 28. Fitting the data of Hg adsorption onto, Purolite A500 CPlus(a), AmberSep 91419 (b) and AC (c) to IPD model.	92
Figure 29. Langmuir and Freundlich isotherms of Au adsorption onto different adsorbents.	94
Figure 30. Elution pre-tests of Hg from Purolite 500CPlus (a), AmberSep 91419 (b) and Activated Carbon (c).	95
Figure 31. Effect of sulfuric acid concentration on Au and Hg elution from Purolite 500Cplus (a) and AmberSep 91419 (b), at 40 BV, retention time 4 hours, temperature 25 °C and shaking speed 200 rpm.	97
Figure 32. Effect of eluent amount (BV) on Hg and Au elution from Purolite 500Cplus (a) and AmberSep 91419 (b), at eluent concentration 2 M, retention time 4 hours, temperature 25 °C and shaking speed 200 rpm.	99
Figure 33. Effect of retention time on Hg elution from Purolite 500Cplus (a) and AmberSep 91419 (b), at eluent concentration 2 M, 40 BV, temperature 25 °C and shaking speed 200 rpm.	100
Figure 34. Effect of temperature on Hg and Au elution from Purolite 500Cplus (a) and AmberSep 91419 (b), at eluent concentration 2 M, 40 BV, retention time 4 hours and shaking speed 200 rpm.	101

Figure 35. Kinetics of Hg elution from Purolite 500Cplus and AmberSep 91419, eluent concentration 0.5 M, 40 BV, temperature of 25°C, and a shaking speed of 200 rpm.	102
Figure 36. Elution pre-tests of Au and Hg from Purolite 500CPlus (a), AmberSep 91419 (b) and Activated Carbon (c).	103
Figure 37. Effect of NaCl concentration on elution of Purolite 500Cplus (a) and AmberSep 91419 (b), at NaClO .75%, NaOH 5 g/l, 40 BV, retention time 12 hours, temperature 40 °C and shaking speed 200 rpm.	105
Figure 38. Effect of NaClO concentration on elution of Purolite 500Cplus (a) and AmberSep 91419 (b), at NaCl 150 g/l, NaOH 5 g/l, 40 BV, retention time 12 hours, temperature 40 °C and shaking speed 200 rpm.	106
Figure 39. Effect of eluent bed volume on elution of Purolite 500Cplus (a) and AmberSep 91419 (b), at NaCl 150 g/l, NaOH 5 g/l, NaClO 0.75%, retention time 12 hours, temperature 40 °C and shaking speed 200 rpm.	107
Figure 40. Effect of retention time on elution of Purolite 500Cplus (a) and AmberSep 91419 (b), at NaCl 150 g/l, NaOH 5 g/l, NaClO 0.75%, BV 40, temperature 40 °C and shaking speed 200 rpm.	109
Figure 41. Effect of temperature on elution of Purolite 500Cplus (a) and AmberSep 91419 (b), at NaCl 150 g/l, NaOH 5 g/l, NaClO 0.75%, BV 40, retention time 12 hours and shaking speed 200 rpm.	110
Figure 42. Kinetics of Au and Ag elution from Purolite 500Cplus (a) and AmberSep 91419 (b). NaCl 150 g/l, NaOH 5 g/l, NaClO 1% v/v, (BV) 80, retention time of 12 hours, temperature 50 °C, and shaking speed of 200 rpm.	112
Figure 43. Purolite A500Cplus resin, SEM pictures for at low magnification for fresh resin (a), one-time eluted resin (b) five time loaded/eluted resin (c).....	117
Figure 44. AmberSep 91419 resin, SEM pictures for at low magnification for fresh resin (a), one-time eluted resin (b) five time loaded/eluted resin (c).....	117
Figure 45. SEM-EDS profile of Purolite A500Cplus after 5 cycles of adsorption/elution	118
Figure 46. SEM-EDS profile of AmberSep 91419 after 5 cycles of adsorption/elution	118
Figure 47. Purolite A500Cplus resin, low magnification SEM pictures for fresh resin (a), Loaded resins (b) one-time eluted resin (c) five time loaded/eluted resin (d).	119
Figure 48. AmberSep 91419 resin, low magnification SEM pictures for fresh resin (a), Loaded resins (b) one-time eluted resin (c) five time loaded/eluted resin (d).	119
Figure 49. FTIR spectra of fresh, loaded, and eluted Purolite A500Cplus resin.	121
Figure 50. FTIR spectra of fresh, loaded, and eluted AmberSep 91419 resin.	122

LIST OF TABLES

	<u>Page No</u>
Table 1. Solubility of some metals in Hg (Marsden and House, 2006).....	9
Table 2. Chemical materials used within the scoop of this study	48
Table 3. Characteristics of the activated carbon	49
Table 4. Physical and chemical properties, and the operating conditions of the resins.	50
Table 5. Different instruments used in within the scoop of this project.	51
Table 6. Chemical composition of the sample.....	54
Table 7. ICP analysis of glycine PLS	55
Table 8. The composition of the synthetic solution	56
Table 9. Properties of the resins used in the screening test.	58
Table 10. Results of the screening test	58
Table 11. Coded and the uncoded values of the parameters.....	59
Table 12. Results of the screening test, resin 1 g/l, pH 10.5, temperature 25 °C, shaking speed 200 rpm.	68
Table 13. Summary of Au and Hg adsorption models	69
Table 14. Analysis of Variance for the adsorption parameters' liner effect, square effect and Two-way interaction on Au and Hg adsorption.....	70
Table 15. Statistical parameters of pseudo -first and -second order models, for adsorption of Au and Hg onto Purolite 500Cplus resin at different Au concentrations.	85
Table 16. Statistical parameters of pseudo -first and -second order models, for absorption of Au and Hg onto AmberSep 91419 resin at different initial Au concentrations.	86
Table 17. Statistical parameters of pseudo -first and -second order models, for adsorption of Au and Hg onto activated carbon at different Au concentrations.	87
Table 18. Statistical parameters of pseudo -first and -second order models, for adsorption of Au and Hg onto Purolite 500Cplus resin at different initial Hg concentrations.	88
Table 19. Statistical parameters of pseudo -first and -second order models, for adsorption of Au and Hg onto AmberSep 91419 resin at different initial Hg concentrations.	89

Table 20.	Statistical parameters of pseudo -first and -second order models, for adsorption of Au and Hg onto activated carbon at different initial Hg concentrations.	90
Table 21.	Langmuir and Freundlich adsorption isotherm parameters for Au adsorption onto different adsorbents	93
Table 22.	Results of Au, Ag and Hg multicycle Adsorption/Desorption conducted on Purolite resin.	113
Table 23.	Results of Au, Ag and Hg multicycle Adsorption/Desorption conducted on AmberSep 91419 resin.	115



LIST OF SYMBOLS AND ABBREVIATIONS

K_1	: First order adsorption rate constant, (1/min)
K_2	: Second order adsorption rate constant, (1/min)
q_e	: Amount of adsorbate at equilibrium, (mg/g)
q_t	: Amount of adsorbate on the surface of the adsorbent at time t, (mg/g)
C_o	: Initial metal concentration, mg/g
C_t	: Metal concentration at time t, mg/g
K_F	: Freundlich adsorption equilibrium constant (mg/g)/(mg/L) ^{1/n}
K_L	: Langmuir adsorption equilibrium constant (l/mg)
K_{id}	: The intraparticle diffusion rate constant
Q_L	: The amount of the metal in the eluent, mg
Q_o	: Amount of the metals adsorbed in the fresh resin, mg
Q_r	: Amount of the metal adsorbed after regeneration, mg
Q_s	: The amount of the metal in the adsorbent, mg
R_L	: Separation factor of Langmuir
q_m	: The maximum adsorption capacity predicted by LAIM (mg/g)
q_t	: Amount of adsorbate on the surface of the adsorbent at time t, (mg/g)
]-	: Polymer matrix and
AARL	: Anglo American Research Laboratories
AAS	: Atomic Absorption
AC	: Activated Carbon
Adj.	: Adjusted
ADR	: Adsorption, Desorption and Recovery
BET	: Brunauer, Emmet, and Teller Theory for Surface Area Measurement
BV	: Bed Volume
CCD	: Central Composite Design
CIC	: Carbon in Column
CIL	: Carbon in Leach
CIP	: Carbon in Pulp
CTC	: Carbon Tetrachloride
DOE	: Design of Experiments

EDX	: Energy-dispersive X-ray Spectroscopy
Eq/kg	: Equivalent/kilogram
FAIM	: Freundlich adsorption isotherm model
FB	: Free Base
FCC	: Face-centred Cubic
FDA	: The US Food and Drug Administration
FG	: Functional Group
FIAS	: Flow Injection for Atomic Spectroscopy
FTIR	: Fourier-Transform Infrared Spectroscopy
GPLS	: Glycine Pregnant Leaching Solution
ICP	: Inductively Coupled Plasma
IPD	: Intraparticle Diffusion
IX	: Ion Exchange
IXOS	: Molecularly Imprinted Resin
LAIM	: Langmuir Adsorption Isotherm Model
LSM	: Large-Scale Mining
MA	: Mixed Amines
MB	: Mixed Base
MR	: Moisture Retention
PEIB	: Polyethylene Imine Modified Biomass
PFO	: Pseudo-First Order
PLS	: Pregnant Leach Solution
Pred.	: Predicted
PSO	: Pseudo-Second Order
QA	: Quaternary Amine
QAm	: Quaternary Ammonium
R	: An alkyl Chain
<i>RE</i>	: Regeneration Efficiency
RIC	: Resin In Column
RIL	: Resin In Leach
RIP	: Resin In Pulp
R-value	: Relative Humidity
SB	: Strong Base

SEM : Scanning Electron Microscopy
TA : Tertiary Amine
TG : Thermal Gravimetric
WAD : Weak Acid
XRD : X-ray Diffraction



1. INTRODUCTION

1.1. Overview

Mining has played a crucial role in human civilization for more than 10,000 years and continues to be an integral part of our modern society. Despite the numerous challenges faced by the industry, it consistently provides essential resources that are necessary for our daily activities (URL-1, 2023). In today's world, artisanal gold mining, commonly known as ASGM, has become a means of livelihood for impoverished individuals in over 70 countries. This industry relies on the use of mercury to recover gold (Hentschel et al., 2002). However, due to the inefficiency of the process, its tailings contain a significant amount of gold, making them a highly profitable secondary resource (Bansah, et al., 2018).

Currently, many companies have begun extracting gold from these tailings using conventional cyanide leaching. It is important to note that the use of cyanide on mercury-containing ores or tailings is prohibited by the Minamata Convention on Mercury (Bansah, et al., 2018). According to Pramudya (2015), this extraction process allows for the recovery of all gold content from the tailings, but only 40% of the mercury can be extracted. Consequently, a huge quantity of tailings containing highly mobile and toxic mercury complexes is released into the environment (Branch, 1994). Despite the hazardous consequences associated with this practice, both companies and individuals continue to employ these methods.

An alternative solution is required to address the problem of recovering Au and removing mercury from these tailings. In recent times, numerous scientific research institutions and international organizations have been diligently working towards finding an effective substitute for cyanide as a lixiviant. Among the successful studies conducted, one achieved a remarkable gold recovery rate of 85.1% using KMnO_4 as an oxidant under leaching conditions of pH 10.5, 1.5 kg/t glycine, and 3 kg/t permanganate with 30% solids (Oraby et al., 2020). This technology was subsequently adopted and patented at Karadeniz Technical University by Kantarcı et al. (2022) for the dissolution of Au and Hg from ASGM tailings. While the leaching process has proven to be highly successful, the downstream processes such as adsorption-desorption and recovery have not yet been thoroughly studied.

On a global scale, there has been a lack of research on the selective recovery of gold and mercury from amino acid leaching solutions. This poses a significant challenge in implementing this innovative technology unless all the downstream processes, including adsorption, desorption, and electro-winning, are optimized. Therefore, this thesis not only introduces novel research topics to the scientific community and fills a substantial gap in the existing literature but also enables the practical application of this new eco-friendly technology. Moreover, it contributes to reducing the release of mercury into the atmosphere, thereby enhancing safety by minimizing mercury exposure rates. From an economic standpoint, this technology will aid in reducing expenses associated with cyanide detoxification. Additionally, the adsorption and desorption of gold and mercury complexes will occur at ambient temperatures, which is considered a highly cost-effective factor.

This work is comprised of six chapters, with the first chapter serving as an introduction that primarily focuses on the aims and problem statement. Chapter two provides a literature review, offering background information specifically on the current practices of gold leaching methods and the dominant processes involved in recovering metal complexes from the PLS, along with well-known elution methods. The third chapter outlines the research methodology employed in the experimental studies, including sample characterization, adsorption optimization process experiments, selective elution experiments, as well as the experimental and analytical procedures for the results. Chapter four presents a comprehensive report on the experimental results and their subsequent discussion. Chapter five encompasses the conclusions drawn from the study, while chapter six delves into recommendations for future work.

1.2. Problem Statement

The gradual increase in gold prices over the past four decades, coupled with the presence of gold-rich deposits that are challenging to exploit even with advanced mining techniques, has prompted individuals in impoverished and underdeveloped regions to consider extracting gold from these deposits through a practice known as artisanal gold mining (ASGM) (Hentschel et al., 2002). The extraction process in ASGM involves the use of the amalgamation technique, which, under optimal conditions, recovers approximately 60% of the gold. However, in certain cases, more than 65% of the gold is lost in the tailings stream (Bansah et al., 2018). These tailings also contain a significant amount of mercury that

has been washed away during the process (Branch, 1994). The current method of cyanidation, which is widely used for gold extraction, is prohibited internationally when mercury is present in the ores or tailings. Therefore, an alternative method must be developed to exploit the gold present in ASGM tailings. Recently, a new method utilizing eco-friendly lixiviants, specifically glycine, has been developed to leach gold and mercury from these tailings resulting in a PLS containing both Au- and Hg-glycine complexes which needs to be selectively separated in the downstream processes. However, the downstream process of adsorption, desorption, and recovery (ADR) has not yet been studied to the best of our knowledge, making the implementation of this new technology challenging. Also, Hg is notorious to be eluted with Au which would generate serious problems. In this regard, the advancement of the adsorption and selective desorption of gold and mercury from glycine pregnant leach solution (PLS) would be a significant step forward in the application of this process.

1.3. Aims and Objectives

The primary aim of this study is to selectively extract gold and mercury from a glycine pregnant solution, which can be either synthetically prepared or obtained from the leaching of an ASGM tailing sample sourced from Cameroon. In order to accomplish this comprehensive objective, the thesis is structured into several smaller objectives as outlined below.

- The initial step involves characterizing the sample to identify its main components and determine the grade of Au and Hg present.
- The subsequent objective is to select suitable adsorbents for the recovery of metals, ensuring their potential for industrial applicability.
- The optimization of the adsorption process is then pursued by conducting tests to evaluate the impact of various factors on the adsorption process. The aim is to identify the parameters that yield the highest recovery of Au and Hg from the pregnant solution.
- The selection of appropriate eluent is another crucial objective, focusing on their ability to selectively elute Au and Hg. In addition to investigation of the effect of multiple parameters on the elution of Hg and Au, with the goal of identifying the conditions that enable complete and selective elution.

- The whole thesis is dedicated to contributing scientifically and technically to the existing knowledge regarding the treatment of mercury-rich gold ores. Finally,
- Providing comprehensive information that facilitates the industrialization of glycine leaching for ASGM tailings.



2. LITERATURE REVIEW

2.1. Introduction

The mining industry has faced criticism in recent years, yet it is imperative to acknowledge its significance in our daily lives. For over 10,000 years, mining has played a fundamental role in the civilization and remains a crucial aspect of modern societies. Despite the obstacles it encounters, industry consistently provides essential resources that are indispensable for everyday activities. Therefore, it is crucial to recognize the importance of mining and support endeavours that foster its sustainability. (URL-1, 2023). Throughout history, the mining industry has played a crucial role in facilitating technological advancements by providing the essential raw materials. Such advancements would have been impossible without the contributions of the mining industry, argued Martens and Rattman (2001). On the other hand, as technology has progressed, the demand for raw materials has increased, leading to a proportional expansion of the mining industry. Among the various mining sectors, the radium, silver, and gold mining sectors have particularly thrived, demonstrating their significance in meeting the growing needs of society (Carvalho, 2017).

The extraction of gold has been a longstanding tradition among human beings, persisting vigorously across the entire world. Despite its association with both favourable and unfavourable political, environmental, and social consequences, the practice has continued to exhibit a gradual upward trajectory since the 1970s. This can be attributed to the significant surge in gold prices and the continuous advancements in exploration and processing technologies (Mudd, 2007).

2.2. Gold Characteristics

The precious metal known as Au is characterized by its bright metallic yellow colour and is highly resistant to corrosion. It is also notable for its considerable malleability and has a high density of 19.32 g/cm³. Additionally, gold has a high melting temperature of 1064°C. In its bulk, metallic form, gold has FCC structure, which has a significant impact on its mechanical, electrical, and other physical properties. This structure also provides an abundance of opportunities for alloying, high ductility, and relativistic induced surface

reconstructions (Corti, 2009). Humans initially turned to gold and copper as their first choice of metals due to their natural occurrence and unique physical properties. These metals possessed the advantageous qualities of being malleable and ductile, allowing them to be easily shaped and manipulated using basic tools. The utilization of gold began during the Neolithic age in what is now known as the Middle East, where it was extracted from streambeds through manual labour or crude gravity concentration techniques. This early acquisition of gold served as a form of currency, with grains and small bars being used for monetary transactions. However, over time, gold's primary role shifted towards adornment and jewellery, a purpose that still holds true in contemporary society (Marsden & House, 2006).

It occurs in various geological settings. Its average abundance in the Earth's crust is estimated to be between 0.003 to 0.004 parts per million (ppm). Typically, gold is found in one of four well-known deposits, which are Sediment-Hosted Disseminated Gold, Volcanic-Hosted Epithermal Deposits, Porphyry Copper-Related Deposits, and Greenstone Gold Quartz Vein Deposits. In addition to its native form, gold can also be found in various minerals such as Tellurides, sulphides, selenates, and silicates (Adams, 2005).

2.3. Gold Mining Industry

In the mining sector, the key stages required to obtain the final product are extraction, beneficiation, and processing. The choice of technique for extracting gold ores, whether it be open pit or underground methods, depends on various factors including the characteristics of the ore body, economic considerations, efficiency, and recovery. Similarly, the selection of gold beneficiation techniques is determined by the ore's characteristics and economic evaluation, with cyanidation, flotation, amalgamation, and gravity concentration being the four main approaches utilized (Branch, 1994). These beneficiation techniques have passed through many stages before they become mature.

In 1300 BC, gold was first discovered and utilized in the Black Sea region. Miners during that time employed sheep's fleeces in sluices to effectively capture gold, marking an early application of surface chemistry in mineral processing. It took another 300 years for the discovery of amalgamation, but its commercial use was delayed until a later period. A significant breakthrough occurred in 560 BC with the development and widespread use of

the fire refining process for gold. By 1400 AD, amalgamation and retorting processes became widely employed in gold extraction (Marsden & House, 2006).

Subsequently, during the 19th century gold rush era, the need for high-capacity processing technologies arose to handle a broader range of ore types on larger scales. This led to the development of various machinery for gravity concentration. Despite advancements in gravity concentration and amalgamation methods, they proved ineffective in recovering fine sulphide gold minerals. As a result, the chlorination process was introduced in the United States, South Africa, and Australia. It was often used to supplement existing gravity concentration circuits or to treat concentrates rich in sulphides. However, due to the high treatment costs resulting in a high gold cut-off (grades around 50 g/t), bromide-cyanide solutions emerged as cost-effective alternatives for treating ores containing Arsenopyrite and/or gold Tellurides between 1900 and the 1920s (Marsden & House, 2006).

Following this period, the gold cyanidation process emerged as the dominant procedure in the gold industry and remains so to this day. However, concerns have recently arisen regarding the high toxicity of cyanide, leading to increased regulatory restrictions and its poor selectivity with low-grade ores. As a result, numerous non-cyanide gold lixiviants such as thiosulfate, glycine, thiourea, halide, and thiocyanate have been proposed and extensively studied as potential alternatives (Oraby et al., 2020).

2.4. Gold Amalgamation

The amalgamation process, which involves the use of mercury to extract gold and silver, was first discovered around 1000 BC. However, it was not widely utilized for gold recovery until much later. In the 19th century, approximately half of South Africa's gold production relied on amalgamation. Nevertheless, the advent of cyanide leaching, along with the associated health concerns, led to a gradual decline in the use of mercury (Marsden & House, 2006). By 1986, reliable statistics indicated that only 0.5% of the total gold production in the USA was achieved through amalgamation. This shift away from mercury-based extraction methods highlights the ongoing efforts to prioritize environmental and health considerations in the mining industry (Branch, 1994).

At ambient temperatures, mercury is commonly found in a liquid state due to its low melting point. Marsden and House (2006) have noted that mercury tends to readily combine with various metals such as sodium, zinc, potassium, gold, and silver, resulting in the

production of amalgam. The process of producing amalgam is often associated with the use of an amalgamation table, where a slurry containing native gold and silver is fed onto a copper plate covered with a thin layer of mercury. The gold and silver adhere to the mercury, producing amalgam that contains approximately 40 - 50% Au as demonstrated in Figure 1. After the distillation and evaporation of mercury, bullion of gold is obtained (Adams, 2016). But in some cases, mercury is removed by washing with hot nitric acid (Branch, 1994).

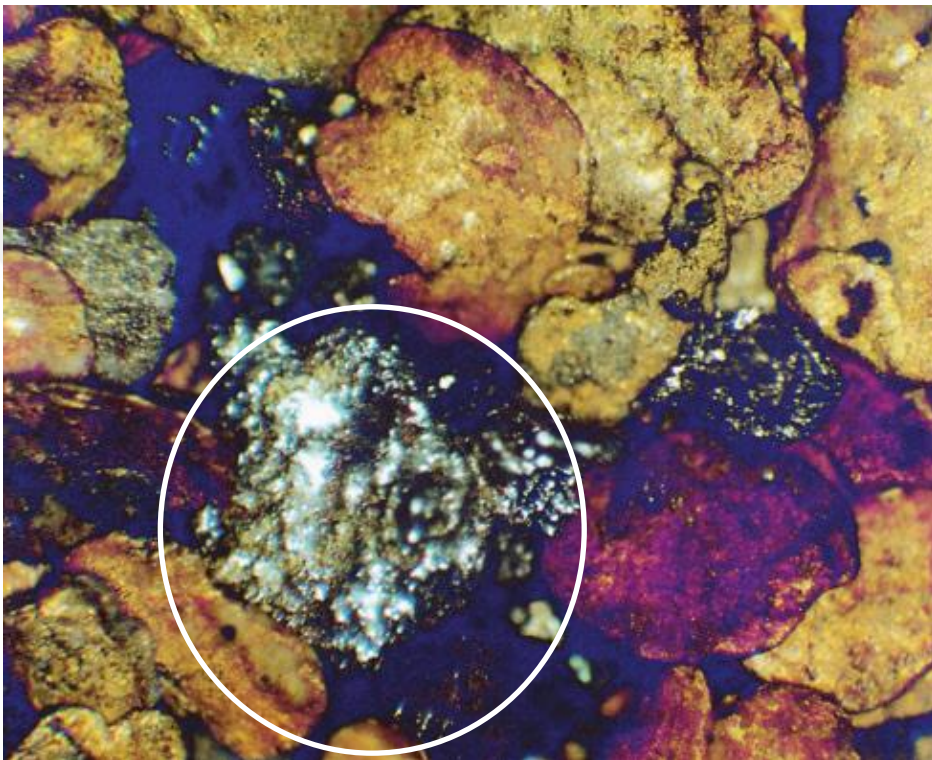


Figure 1. Gold and silver amalgamation (Marsden & House, 2006).

Several factors must be considered for the effective recovery of gold through amalgamation. Achieving sufficient metal exposure to mercury requires adequate grinding and the liberation of metal grains. The interaction between water and mercury, characterized by high surface tension, is also crucial for the successful inclusion of gold in mercury. Additionally, the size of gold grains significantly influences the amalgamation process, as particles smaller than $50\mu\text{m}$ exhibit poor amalgamation. The presence of an oxidizing pulp can negatively impact the quality of mercury and subsequently reduce the efficiency of the process. Moreover, the mineralization of gold and the presence of gangue minerals can greatly hinder amalgamation, particularly when gold occurs in the form of tellurides and

selenide. The existence of sulphide minerals and sulphur further impedes the process by forming highly insoluble HgS according to Equation (1). Lastly, the presence of other mercury-soluble metals presented in Table 1 can create a competitive environment, leading to the consumption of mercury in side reactions (Marsden & House, 2006).



Table 1. Solubility of some metals in Hg (Marsden and House, 2006)

Metal	Solubility (wt.% Hg)
Antimony	2.9×10^{-5}
Barium	0.33
Bismuth	1.4
Copper	2×10^{-3}
Gold	0.13
Indium	27
Iron	1.5×10^{-6}
Lead	1.3
Silver	0.042
Sodium	0.68
Thallium	42.8
Tin	0.62
Zinc	2.15

In optimal circumstances, around 60% of the gold can be effectively recovered through this process. However, there are instances where over 65% of the gold, denoted as Au, is not successfully captured and instead ends up in the tailings stream, as highlighted by (Bansah et al., 2018). Furthermore, it is important to note that these tailings also harbour a significant quantity of mercury, which has been carried away during the course of the process (Branch, 1994).

Although mercury is one of the most toxic heavy metals, its poisonous effects may not be immediately apparent. This delayed onset of symptoms, coupled with its relatively low cost compared to gold, has led to the widespread use of amalgamation in artisanal gold mining (ASGM) in developing countries. Unfortunately, the mercury used in this process can be highly dangerous, as it can either evaporate or runoff into underground water sources. Once in the water, specific types of bacteria can transform the mercury into even more harmful organometallic compounds, such as methyl-, ethyl-, and phenyl-mercury, which can ultimately end up in the ecosystem (Kozin & Hansen, 2013).

2.5. Artisanal Gold Mining Industry

Over the past four decades, there has been a gradual rise in the value of gold as presented in Figure 2 (URL-2, 2023), making it a highly sought-after commodity. Additionally, certain regions have been identified as having abundant deposits of gold, which pose challenges for extraction even with advanced mining methods. As a result, individuals in impoverished and underdeveloped areas have turned to artisanal gold mining (ASGM) to improve their living conditions. This practice involves extracting gold from these deposits using minimal mechanization, allowing for a more accessible and sustainable livelihood for these communities (Hentschel et al., 2002).

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). Despite its ambiguous definition, ASGM has emerged as a significant economic contributor at both the individual and global levels. It employs approximately 20 million miners across seventy countries and provides income for around 100 million individuals. Additionally, it accounts for approximately 20% of the world's total gold production, equivalent to 400 tons of gold per year (Marshall et al., 2020).

ASGM, despite its aforementioned benefits, has gained notoriety for its adverse effects on the environment, occupational health, and safety. This is primarily due to the utilization of mercury amalgamation in the process of gold extraction (Stoffersen et al., 2019). In fact, ASGM stands as the largest contributor to mercury pollution in both water and air on a global scale, accounting for approximately 37% (2058 tons) of the total mercury emissions into the

environment (Marshall et al., 2020). Previous studies made before 2006 have estimated that ASGM releases around 1000 tons of mercury annually (Veiga et al., 2006). However, the actual amount emitted surpasses this estimation (Suliman et al., 2007). Research indicates that if 20 grams of mercury is used to recover 1 gram of gold, 95% of the mercury will end up in the tailings, while the remaining portion is released into the atmosphere (Ilyas & Lee, 2018). This substantial quantity of mercury serves as a strong indication that millions of tons of ASGM tailings are generated each year. Furthermore, since mercury can only recover up to 60% of the gold under optimal conditions, a significant amount of gold is also reported to be present in the tailings.

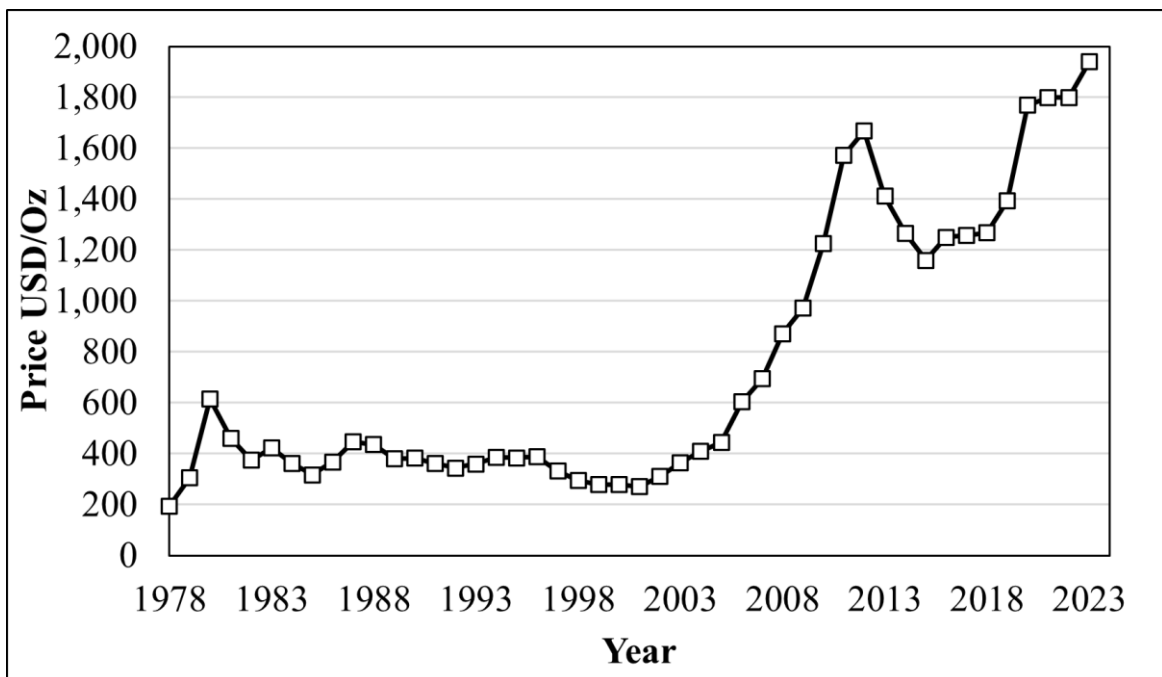


Figure 2. Gold prices in the last four decades in USD/Oz (URL-2, 2023).

The Minamata Convention was established to safeguard the economic value of the mining industry while minimizing the negative impact of mercury consumption. The convention's seventh article mandates all participating countries to reduce or eliminate the use of mercury and its compounds in mining activities. Despite this, the implementation of the agreement has encountered challenges. For instance, in South America, 31 out of 128 member countries have been involved in mercury trade with Mexico, and a significant amount of this trade has gone underground since 2018 (Marshall et al., 2020). This suggests

that the convention's enforcement is problematic, and alternative measures should be explored instead of relying solely on mercury sanctions.

2.5.1. Harmful Effects of Mercury

Exposure to heavy metals such as Hg, Pb, and As has become a significant global health concern (Mostafazadeh et al., 2013). Extensive toxicology studies have established that both inorganic and organic forms of mercury can have severe health effects. Through physical, chemical, and biological transformations, mercury poses a chronic threat to humans by infiltrating the food chain (Kozin & Hansen, 2013). According to a report by URL-3, (2015), approximately 20 million individuals have been diagnosed with health risks associated with mercury pollution, and there are over 450 locations worldwide where mercury pollution levels are dangerously high (Budnik & Casteleyn, 2019) .

All its forms are highly toxic (Mostafazadeh et al., 2013). Even a small amount of mercury is sufficient to cause lifelong health damage (Lee & H. Culter, 2019). The maximum allowable amount of mercury in the human body is 10^{-6} % of the individual's total weight, primarily accumulating in the kidneys and liver to a lesser extent. When this threshold is exceeded, symptoms of mercury poisoning manifest (Kozin & Hansen, 2013). Unlike ordinary poisons, mercury poisoning can interfere with various metabolic processes and give rise to a wide range of symptoms, including psychological, neurological, and physical manifestations (Lee & H. Cutler, 2019). The specific symptoms depend on the type of mercury compound involved (Kozin & Hansen, 2013). The US Food and Drug Administration (FDA) states that chronic mercury poisoning can be diagnosed based on symptoms such as irritability, shyness, tremors, changes in vision or hearing, memory problems, depression, and numbness or tingling in the hands, feet, or around the mouth (Lee & H. Cutler, 2019).

Mercury has been found to have detrimental effects on mammalian organs, as documented by Mostafazadeh et al. (2013). When an individual becomes intoxicated with organic mercury, such as methylmercury, it quickly enters the bloodstream and brain tissue upon entering the body. This can lead to a loss of spatial orientation and partial loss of eyesight, as observed by Kozin and Hansen (2013). Once in the bloodstream, it takes approximately 4-6 days for mercury to be fully distributed throughout the tissues and brain (Nabi, 2014), as depicted in Figure 3 (Subeshan et al., 2023). On the other hand, long-term

exposure to mercury vapor at concentrations of 0.6-2 ppb can result in Acute mercury vapor poisoning. This condition is characterized by disruptions in calcium digestion, alterations in blood proteins, and severe damage to the liver, kidneys, brain, and spleen due to the accumulation of mercury, as explained by Kozin and Hansen (2013).

In developing countries, millions of people are practicing ASGM as it is the only avenue to sustain their livelihood. This practice ends up releasing mm-sized mercury drops, which account for about 40% of the world's mercury pollution (Appel & Esbensen, 2019). It is very enough to make the surrounding mercury content extremely above the tolerable international limits which is 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 & Hansen, 2013).

A study conducted by Mostafazadeh et al. (2013) found that both ASGM workers and employees at small- and full-scale companies that rely on ASGM tailings are exposed to high levels of various forms of mercury. The study measured the concentration of Hg in the blood and urine of 16 gold miners and found that the mean blood and urine mercury levels were 208.14 ppb and 134.70 ppb, respectively. These levels are significantly higher than the reference levels of blood and urine mercury, which are determined to be ≤ 10 ppb and ≤ 20 ppb, respectively (Onwuzuligbo et al., 2018). These findings were supported by a comparative study conducted by Tayrab, et al. in 2016, which measured the serum mercury concentration in 123 individuals, 83 of whom were from the Abu-Hama gold mining region and the rest were from the capital, which is far from ASGM areas. The results showed a substantial increase in the mercury concentrations in gold miners (24.9 ± 32.24 ppb) compared to the other group (1.40 ± 0.94 ppb) (Tayrab et al., 2016). This indicates that not only are miners and their family members exposed to high levels of mercury, but also embryos and fetuses, as mercury has been reported by Nabi (2014) to accumulate in the umbilical cord.

The ASGM industry is a major source of mercury pollution, primarily because mercury is not efficient in recovering the gold. Therefore, the tailings from this industry still contain significant amounts of gold that can be economically valuable. This makes them a profitable secondary resource, especially since they often do not require crushing or grinding. Currently, numerous companies have begun extracting gold from these tailings through conventional cyanide leaching method.

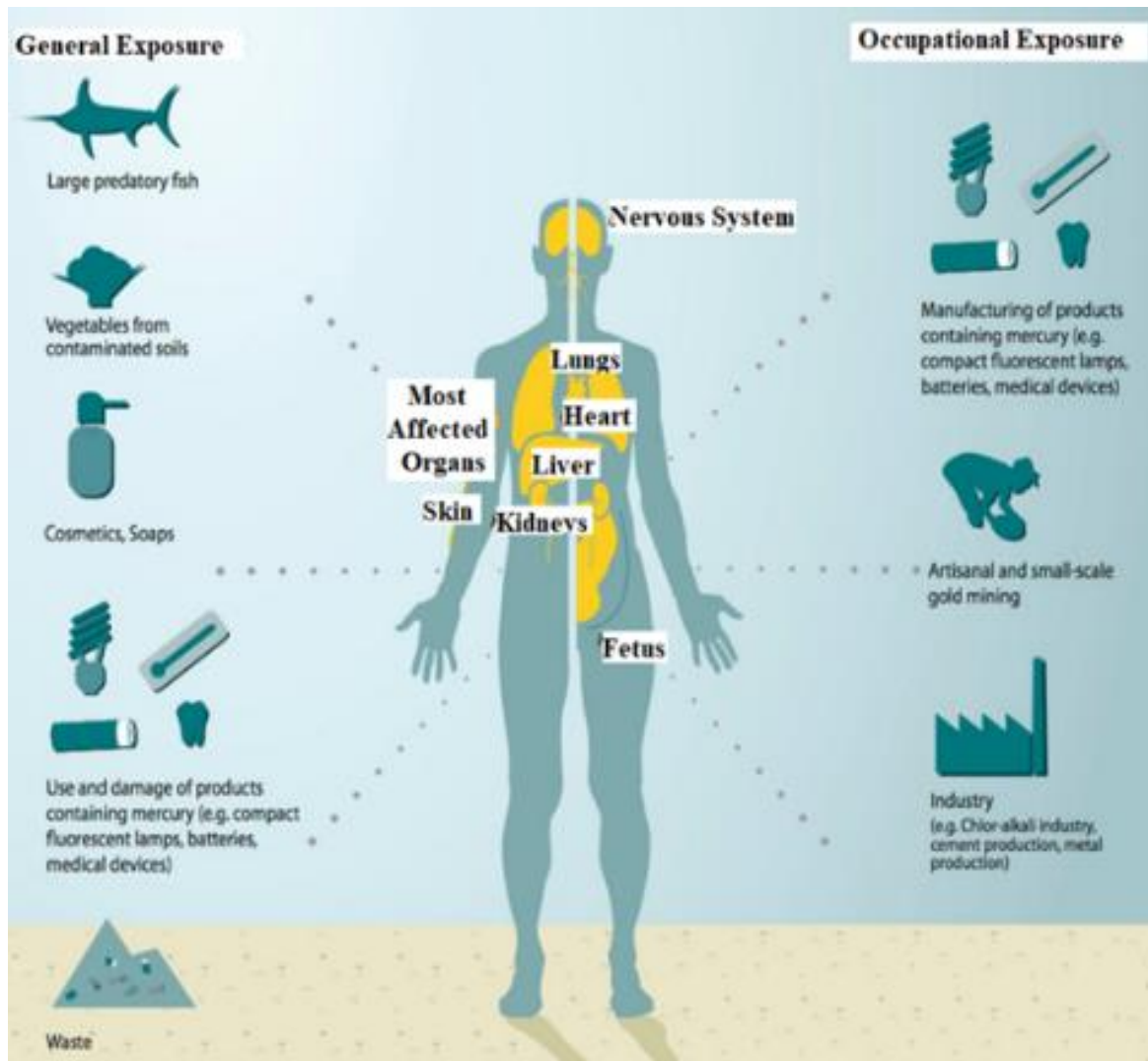


Figure 3. Accumulation of mercury in human's body (Subeshan et al., 2023).

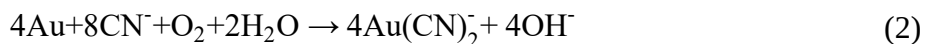
2.6. Gold Leaching Process

For many years, the gold industry has heavily relied on cyanide as the primary lixiviant for extracting gold. However, this approach has encountered significant challenges due to the drawbacks associated with cyanide. These challenges include its high toxicity, increasing regulatory restrictions, and limited effectiveness with low-grade ores. As a result, researchers have been exploring alternative non-cyanide lixivants, such as Thiosulfate, glycine, thiourea, halide, and thiocyanate. While some of these alternative methods have shown technical success, they have also presented their own set of challenges. These challenges include high cost, excessive reagent consumption, and often a low leach rate or

complex downstream recovery process. Despite these limitations, recent research has highlighted the potential of amino acids as a promising alternative for cyanidation. Therefore, in this section, we will delve into a discussion of these two methods: cyanide and amino acids. By examining their advantages, disadvantages, and potential applications, we can gain a better understanding of the viability of amino acids as a substitute for cyanide in gold extraction processes.

2.6.1. Cyanide 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 total global cyanide production, employing highly water-soluble forms of KCN and NaCN (Birich et al., 2019). The mechanism behind gold dissolution in cyanide involves an electrochemical process, where sodium cyanide solutions with low concentrations (100-500 ppm) are used for gold recovery (Syed, 2012). Oxygen is a crucial component in this process, as its presence is necessary for gold dissolution. To prevent the formation of volatile hydrogen cyanide (HCN), the process is carried out in a basic solution with a pH of 10.5. Figure 4 illustrates the speciation of CN^- and HCN as a function of pH (Birich, et al., 2019). It is important to maintain a pH level above 9.21, as the dissociation constant pK_a of HCN at 25 °C is 9.21 (Estay, 2018). Under these conditions, an average dissolution rate of $1.032 \text{ mg}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ and an average gold extraction rate of over 90% can be achieved. The gold is extracted in the form of a dicyanoaurate complex, as shown in Equation (2) (Birich et al., 2019).



In a study conducted by Azizi and Ghaedrahmati (2015), a modelling program was used to analyse the impact of various factors on gold recovery, including pH, solid percentage, NaCN concentration, particle size, and leaching time. The modelling results indicated that under specific conditions (pH 10.11, solid ratio of 36.07%, NaCN concentration of 729.56 ppm, particle size of 37.52 μm , and leaching time of 23.2 h), approximately 91.5% of the gold can be successfully recovered.

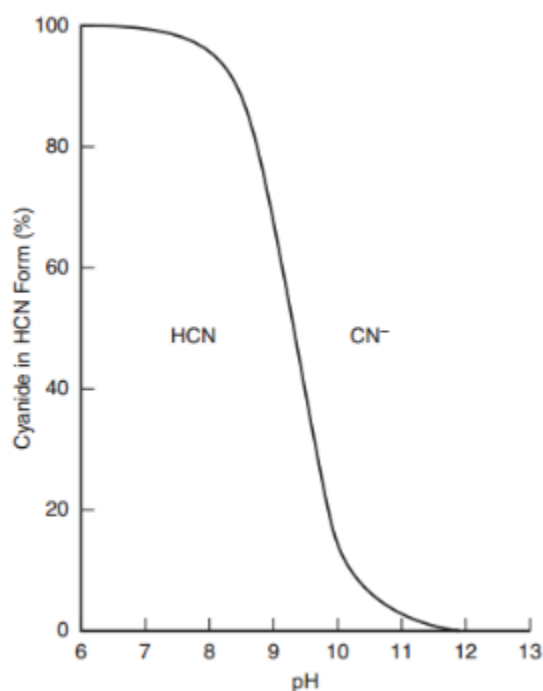
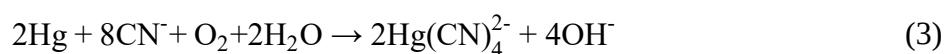


Figure 4. Speciation of cyanide and hydrogen cyanide in aqueous solution as a function of pH (Marsden & House, 2006).

Cyanide ions can form complexes with various metals and molecules, apart from Au and Hg. Some of these complexes, known as weak acid or WAD cyanide, break down and release free cyanide ions when the pH is lowered. On the other hand, strong cyanide complexes such as gold, cobalt, and iron cyanide complexes degrade at a much slower rate under natural conditions (Hilson & Monhemius, 2006).

In addition to ASGM tailings, gold-bearing ores often contain small amounts of mercury (Sandberg et al., 1984). As shown in Equation (3), mercury can be leached out along with gold under optimal leaching conditions. According to Pramudya (2015), the extraction of mercury can reach up to 40% depending on the cyanide concentration and the degree of mercury liberation. Furthermore, de Andrade Lima, Bernardez et al. (2008) reported a 100% recovery of mercury from ASGM tailings containing 1.8 and 10 ppm of Au and Hg respectively (de Andrade Lima, et al., 2008). However, the accuracy of these results is questionable due to the lack of information regarding the specific optimal conditions under which these results were achieved.



The cyanide leaching process has encountered significant challenges in recent years, despite its advantages such as its effectiveness in extracting gold and the stability of its complexes (Adams, 2005). Environmental incidents at gold mines worldwide (Hilson & Monhemius, 2006; Syed, 2012) and the focus on refractory ores that hinder efficient gold extraction using cyanidation, have raised concerns about the use of cyanide (Birich et al., 2019). As a result, the industry has been exploring alternative methods to facilitate faster gold recovery rates, including thiourea, thiosulfate, thiocyanate, halides, and coal-oil agglomeration (Hilson & Monhemius, 2006; Syed, 2012).

Additionally, there has been a growing trend among major mining operators to invest in the tailings of artisanal and small-scale gold mining (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 & Hansen, 2013), which can easily contaminate inland water through methylation and runoff (Ilyas & Lee, 2018). To address this issue, the Minamata convention was convened, with its seventh directive urging all participating countries to take measures "to eliminate the use of cyanide leaching in sediment, ore or tailings to which mercury has been added without first removing the mercury." Nevertheless, the implementation of this convention has proven challenging, particularly in developing nations where mercury continues to be used (Marshall et al., 2020). Moreover, large-scale mining companies (LSM) face difficulties in completely abandoning cyanide due to its well-established effectiveness and cost-efficiency as a leaching method for gold. Consequently, the search for a viable alternative to cyanide remains a crucial priority.

The outcomes from the experimental study have indicated that the utilization of thiourea and thiosulphate relates to substantial expenses for detoxification, limited ability to be recycled, and challenges in controlling the process parameters. Despite its notable stability, the application of thiocyanate encounters significant obstacles that impede its potential as an alternative option. Furthermore, halides are known to be costly and pose difficulties in handling (Hilson & Monhemius, 2006). In order to address this issue, the use of organic ligands as a substitute for gold leaching has been proposed. Researchers at Curtin University have introduced and patented the use of glycine and other amino acids, such as glutamic acid, as lixivants for both base and precious metals. This proposed alternative not only resolves the environmental shortcomings but also competes with cyanide in terms of cost and technical efficiency (Oraby et al., 2020).

2.6.2. Gold Leaching with Amino Acids

The research conducted by Adams (2016) has provided information on the solubility of gold in organic systems, specifically microorganisms and organic acids, in an oxidizing environment. These organic acids encompass a range of compounds such as amino acids, carboxylic acids, nucleic acids, proteins, and peptides. It has been observed that these organic acids exhibit varying abilities to form complexes with gold, with cysteine demonstrating the highest affinity, followed by histidine, asparagine, methionine, glycine, alanine, valine, and phenylalanine. The formation of stable complexes between these organic acids and gold is attributed to the presence of nitrogen atoms in the amino group and oxygen atoms in the carboxyl group (Jorjani & Sabzkoohi 2021), when amino acids react with gold in the presence of an oxidant, the resulting product is a complex anion consisting of Au(I) and a salt of the amino acid, connected through the Au-N bond.

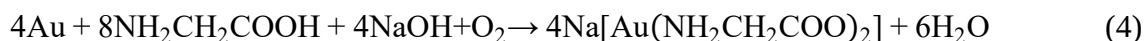
Eksteen and Oraby (2015) conducted a study to investigate the complexation of gold by different amino acids, using hydrogen peroxide as an oxidant. The findings of the study revealed that even at low concentrations, amino acids could form complexes with gold within timeframes that are suitable for in-situ or heap and vat leaching processes. Despite its sensitivity to temperature, glycine exhibited higher reaction kinetics when compared to other amino acids. As a result of these findings, glycine has been selected for further research on the complexation of gold, copper, and other metals.

2.6.3. Glycine Leaching

Glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) is an amino acid that is stable and has various aqueous ionic forms. These forms include the cationic glycinium ion in acidic solutions ($\text{NH}_3\text{CH}_2\text{COOH}^+$), the neutral zwitterion ($\text{NH}_3\text{CH}_2\text{COO}^-$), and the anionic glycinate ($\text{NH}_2\text{CH}_2\text{COO}^-$) ion in alkaline solutions. It is demarcated by two pKa values at 2.34 and 9.6. It has a high solubility in water at around 250 g/l at 25°C, a density of 1.607 kg/t, a molar mass of 75.07 g/mol, and a melting point of 233°C (Eksteen et al., 2018).

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. However, even at elevated temperatures, its leaching rate is not adequate. The use of a strong oxidant such as hydrogen peroxide and the addition of a small amount of catalytic or synergistic metal ions to the system can improve the performance of the lixiviant (Eksteen et al., 2018).

The stoichiometry of gold dissolution in alkaline glycine solutions is generally described in Equation (4) (Eksteen & Oraby, 2015).



In their study on the intermolecular interaction between Au and glycine using density functional theory (DFT), Xie, et al., (2012) presented six potential geometry patterns for the Au-glycine complexes, as shown in Figure 5. Their findings revealed that the complexes with an Au-NH₂ anchoring bond (1 & 4) were more energetically favourable than the other possible complexes of Au-O and Au...H-O, (2 & 5) and (3 & 6) respectively.

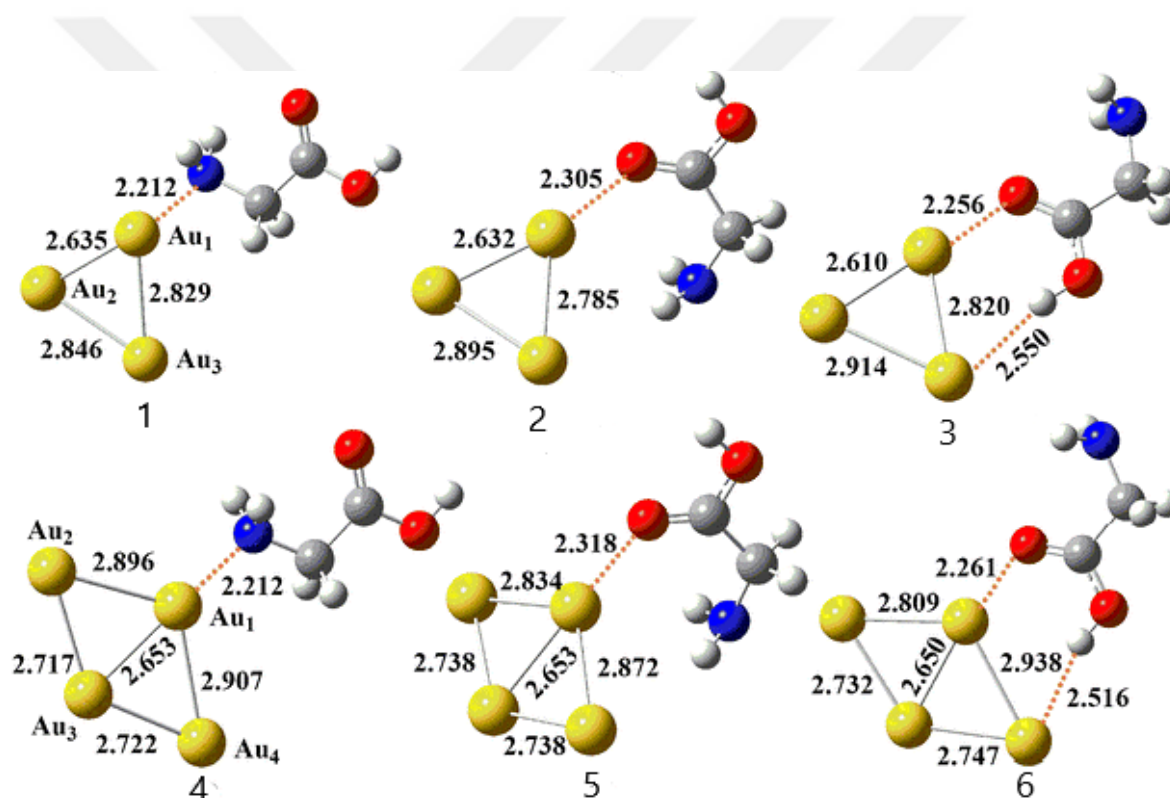


Figure 5. Optimized geometries of Au- Glycine complexes (Xie, et al., 2012).

In comparison, glycine offers numerous benefits in contrast to cyanide and its substitutes. It is environmentally friendly and can be manufactured in large quantities in industrial settings, making it comparable to cyanide while being significantly more cost-effective than other alternative lixivants. Additionally, its complexes exhibit stability across a broad range of pH and Eh values as it is shown in Figure 6. As a result, the depleted

glycinate solution can be recycled and reused after metal recovery, which makes it viable sustainable (Eksteen et al., 2018).

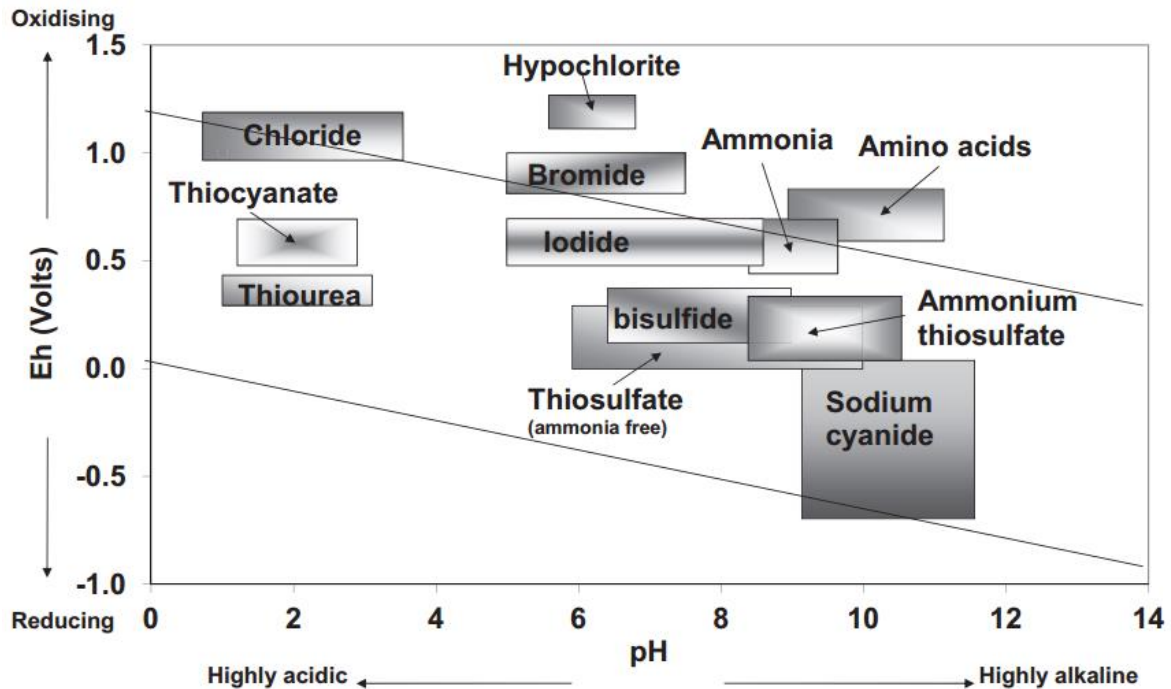


Figure 6. Eh-pH diagram showing typical operating regions for gold lixiviants (Adams, 2016).

Numerous investigations have been conducted on glycine since it was identified as a promising agent for extracting valuable metals, with the aim of determining the optimal conditions for the extraction process. In a study by Eksteen, et al. (2018), the impact of pH, temperature, glycine concentration, and hydrogen peroxide concentration on the dissolution of pure gold was examined. The most favourable leaching rate of $0.322 \mu\text{mol m}^{-2} \text{s}^{-1}$ was achieved at a pH of 11 and a temperature of 60°C , using a glycine concentration of 0.5 M and 1% hydrogen peroxide. However, it is important to note that this leaching rate is still only about one-third of the leaching rate achieved with cyanide, despite the high temperature and reagent concentration employed in the study. (Azadi et al., 2019) suggested that higher gold leaching rates can be achieved by increasing the temperature to 75°C and the pH to 11. This claim is supported by Oraby and Eksteen (2015), who attributed the increase in leaching rates at high temperatures to the fact that of the reaction between gold and glycine is chemical-controlled, and the increase in gold dissolution at high pH to the activation of hydrogen peroxide by caustic soda. They also noted that the leaching rate at high pH

decreases over time due to the passivation of the gold surface by OH^- ions (Oraby & Eksteen, 2015). Conversely, Altinkaya (2020) achieved a recovery of 90% Au at a pH of 12 and a temperature of 60 °C, using a leaching solution containing 1.25 M glycine within a leaching time of 24 hours.

Despite the high leaching temperature and glycine concentration employed in previous experiments, the leaching rates were found to be significantly lower than those achieved through cyanide leaching. In view of this, a study was conducted by (Oraby et al., 2019) to explore the potential of using glycine in heap and in-situ leaching. The study revealed that a recovery rate of 85% could be achieved after 2 weeks of leaching using 15 g/l of glycine at a leaching temperature of 40 °C, which was found to be more cost-effective than previous studies conducted at higher temperatures and glycine concentrations. However, the amount of glycine used was still considerably higher than that used in cyanide leaching, indicating the need for further research in this area. Oraby, et al. (2020) investigated the impact of various oxidants including potassium permanganate, hydrogen peroxide, sodium chlorate, potassium iodide, and potassium ferricyanide, on gold recovery from oxide ore. The highest gold recovery rate of 85.1% was achieved using potassium permanganate as an oxidant under leaching conditions of pH 10.5, 1.5 kg/t glycine, and 3 kg/t permanganate at 30% solids. These results represent a significant advancement in the field, as the reagent concentration is much lower compared to previous studies and can be economically compared to those of cyanide leaching. This method can be used to address the issue of the artisanal mining tailings since it adopts an environmentally friendly lixivants usage.

Youpoungam A. A., (2023). conducted a study to address the environmental concerns associated with the use of cyanide in processing mercury-bearing ASGM tailings. The study utilized a Glycine-potassium permanganate system to dissolve gold and mercury from an oxide ASGM tailing sourced from Sudan. The researchers investigated the impact of various factors such as temperature, pH, and concentration of the lixiviant and oxidant on the leaching process. The study found 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, more than 90% of the gold and mercury were recovered within 8 hours. The outcomes of this study are highly innovative and have the potential to offer an eco-friendly process alternative solution for the utilization of cyanide in the extraction of gold from ASGM tailings. In addition to the sustainable elimination of mercury from the tailings. The same process was patented by Kantarcı et al., (2022)

Based on the findings presented, the leaching process of Au and Hg from ASGM (Artisanal and Small-Scale Gold Mining) has reached a highly satisfactory level, except for the monitoring process involving glycine and potassium permanganate. However, in order for this process to be implemented on an industrial scale, further optimization is required for downstream processes such as the recovery of precious metals, tailing disposal, and visibility studies. Therefore, this thesis aims to investigate the selective recovery of gold and mercury from glycine pregnant leaching solution (GPLS). This study is innovative and has the potential to pave the way for a gradual shift from cyanidation to a more environmentally friendly gold production process. Additionally, the results acquired from this study can be applied for both ASGM tailings and natural mercury-bearing gold ores, which will ultimately lead to the elimination of mercury-contaminated tailings being released into the environment.

2.7. Recovery of Gold and Mercury from PLS

Following the leaching process, the solution containing the complexes is commonly known as the pregnant leach solution (PLS). To concentrate and purify the precious metals, various methods such as solvent extraction, cementation, and adsorption are employed (Azizitorghabeh et al., 2021). In the adsorption process, the valuable metal is initially adsorbed from the diluted PLS onto an adsorbent like AC or ion exchange resin (IX). Subsequently, the loaded adsorbent is eluted using a small quantity of a suitable eluant, resulting in a concentrated solution suitable for downstream processes (Marsden & House, 2006). The same principle is applied in solvent extraction, with the key distinction being the use of organic liquid as the solvent instead of solid adsorbents.

2.7.1. Activate Carbon Adsorption

AC is carbon that has undergone physical or chemical treatment to enhance its properties. This activation process results in AC having a large surface area, high porosity, and increased reactivity and affinity towards aurocyanide ions (Xia et al., 2022). The use of AC for adsorbing precious metal ions or complexes from aqueous solutions was first observed in the early 19th century, during a time when gold recovery primarily relied on zinc precipitation (Marsden & House, 2006). Through continuous research, McQuiston and Chapman officially patented AC as an aurocyanate adsorbent in 1951. Today, it is

commercially employed as carbon-in-pulp (CIP) and carbon-in-leach (CIL) methods to recover gold from both primary and secondary solutions (Oraby & Eksteen, 2015). Furthermore, AC has been found to be effective in gold recovery from cyanide complexes, as well as from thiocyanate, thiourea, and glycine's (Marsden & House, 2006).

Scientists have been engaged in a significant debate about the adsorption mechanism of the aurocyanide complex onto AC, despite its commercial success (Adams, 1990). Different theories, such as ion pair, ion exchange, and simple electrostatic attraction, have been proposed to explain these mechanisms (Xia et al., 2022). The occurrence of these mechanisms depends on the nature of the PLS. In high ionic strength solutions, the adsorption occurs through the ion pair mechanism, where ion pairs of $Mn^+[Au(CN)_2]^-$ type are adsorbed onto the AC surface. However, in low ion strength environments, both ion pair and ion exchange mechanisms are possible. The adsorption of complexes onto AC is also influenced by atmospheric gas. In the presence of oxygen, the ion pair mechanism dominates, while in the presence of nitrogen, the electrostatic ion exchange between unpaired $Au(CN)_2^-$ and the functional group on the surface of AC occurs (Adams, 1990). The adsorption behaviour of the Au-glycine complex is reported to be similar to that of the aurocyanide complex (Oraby & Eksteen, 2015). However, there is currently no study focused on investigating the adsorption mechanism of the gold-glycine complex onto any type of adsorbent.

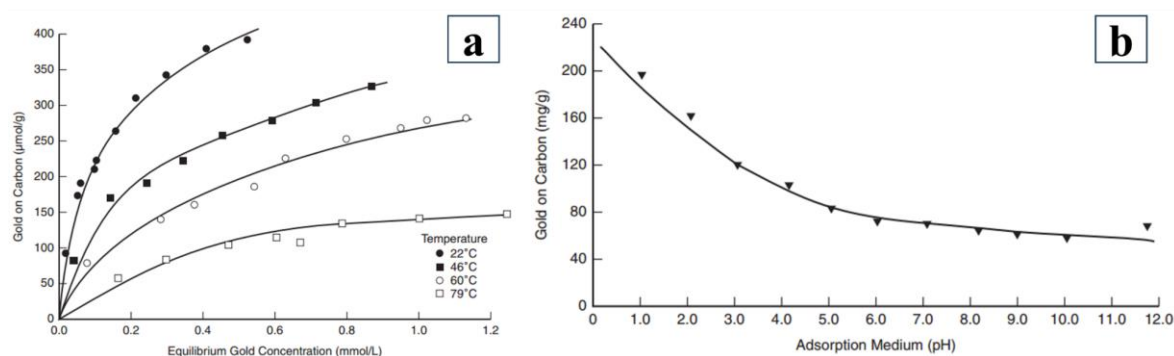


Figure 7. Effect of temperature (a), and pH (b) on aurocyanide adsorption onto AC (Marsden & House, 2006)

The adsorption of the gold-cyanide complex onto AC is influenced by various physical and chemical factors. Physical factors include the type of activated carbon, carbon particle size, mixing efficiency, and the solid content in the pregnant leach solution (PLS). Chemical

factors that affect adsorption include temperature, gold concentration, pH, ionic strength, and the concentration of other metals. It is important to note that gold adsorption onto AC is an exothermic process, meaning that an increase in temperature negatively impacts adsorption as presented in Figure 7. Similarly, an increase in cyanide concentration and the presence of other metal complexes also hinder adsorption due to increased competition for active sites. Conversely, an increase in gold concentration, ionic strength, and a decrease in pH have a positive effect on adsorption (Marsden & House, 2006).

PLS composition can vary and may include different metal ions and complexes such as silver, copper, nickel, zinc, iron, and mercury. These compete with gold for absorption onto activated carbon's active sites, with the affinity of activated carbon towards common metal complexes listed as $\text{Au}(\text{CN})_2^- > \text{Hg}(\text{CN})_2^- > \text{Ag}(\text{CN})_2^- > \text{Cu}(\text{CN})_3^{2-} > \text{Zn}(\text{CN})_4^{2-} > \text{Ni}(\text{CN})_4^{2-} \gg \text{Fe}(\text{CN})_6^{4-}$ according to Marsden and House (2006).

Activated carbon is a preferred method for gold recovery in industry due to its cost-effectiveness, simplicity, and high removal capacity resulting from its large surface area (Tauetsile et al., 2018). This method can successfully recover gold from cyanide, cyanide-glycine, and cyanide-free glycine PLSs. This was supported by a study has been conducted by Oraby and Eksteen (2015), to evaluate the adsorption of (gold & silver)-glycinate onto activated carbon from a solution containing 1M glycine at pH 10, and temperature of 25 °C, about $13.2 \text{ kg}_{(\text{Au})}/\text{t}_{(\text{AC})}$ and $3.5 \text{ kg}_{(\text{Ag})}/\text{t}_{(\text{AC})}$ have been respectively loaded within 4 hours. Tauetsile (2018) also studied the effect of free glycine concentration, solution pH, initial gold concentration, copper concentration, and calcium chloride concentration on the activated carbon adsorption of gold from cyanide-starved glycine synthetic solution. The results showed that the adsorption capacity of activated carbon was positively affected by the free glycine, copper, and calcium chloride concentrations, but negatively affected by solution pH and initial gold concentration. Another study by Tauetsile (2019) demonstrated that about 99% and 52.8% of gold and copper, respectively, can be recovered from a cyanide-glycine PLS containing 2 mg/L Au, 300 mg/L Cu, 5 g/L glycine, and 123 mg/L CN^- within an adsorption time of 6 hours and pH 11.

The recovery of gold from Au-glycine PLS that contains competitive ions like copper and silver has been successfully demonstrated through various studies on AC. However, when glycine is used to leach gold from ASGM tailing, the resulting PLS contains mercury complexes. This poses a challenge as the neutral mercury cyanide complex $\text{Hg}(\text{CN})_2$,

competes directly with $\text{Au}(\text{CN})_2^-$ for adsorption sites on AC, and can even displace some of the adsorbed gold from carbon.

The adsorption mechanisms of gold-cyanate and gold-glycinate onto AC are similar, as reported by Oraby and Eksteen (2015). Marsden and House (2006) also noted the similarities between these mechanisms. Based on these similarities, it is assumed that mercury-glycinate complexes can also be easily adsorbed onto AC, making it difficult to achieve selective adsorption. These findings highlight the need for further research to develop more effective methods for selective adsorption of gold from PLS containing mercury complexes.

To achieve selectivity, it is common practice to elute loaded mercury before gold (Marsden & House, 2006). However, achieving complete elution from AC is challenging. Moreover, the elution of mercury alongside gold can lead to contamination of downstream equipment (Adams, 2005). Furthermore, the high pressure and temperature required for satisfactory gold elution can result in significant environmental issues due to the evaporation of the remaining mercury in AC. Adding to that the carbon reactivation process, which are not only economically burdensome but also environmentally detrimental. These challenges associated with the AC adsorption process have prompted the industry to explore alternative adsorbents that can effectively mitigate economic and environmental costs. One such alternative is ion exchange resin, which offers numerous advantages over AC, as will be discussed in detail in the subsequent section.

2.7.2. Ion Exchange Resin Adsorption

Ion exchange resins (IX) are synthetic materials composed primarily of an inert matrix, such as polystyrene divinylbenzene co-polymers (Adams, 2005; Marsden & House, 2006). These resins can exist in two forms: gel or macroporous. Gel resins are transparent, glassy beads that allow light to pass through, while macroporous resins consist of a gel matrix with a grid-like structure of pores (Van Deventer, 2014). The surface of these resins contains functional groups, such as amines and esters, which facilitate the exchange of ions with similarly charged complexes and ionic species in solutions. Classification of ion exchange resins can be based on their basicity, dividing them into anion exchange (basic) or cationic exchange (acidic). Additionally, they can be further classified as strong, medium, or weak-base resins (Adams, 2005; Marsden & House, 2006).

The active sites of strong-base IX resins primarily comprise quaternary amines, with a smaller presence of tertiary amines. These active sites possess a temporary positive charge, which makes them unaffected by changes in the pH. The production process of these resins involves combining a chloromethylated polystyrene matrix with a tertiary amine, as depicted in Equation (5). Despite their high stability across a broad pH range, conventional strong base resins exhibit poor selectivity for gold over base metals-cyanide complexes. However, this selectivity can be improved by reducing the pH and causing the base metals-cyanide complexes to precipitate out as in Figure 8 (Adams, 2005; Marsden & House, 2006).

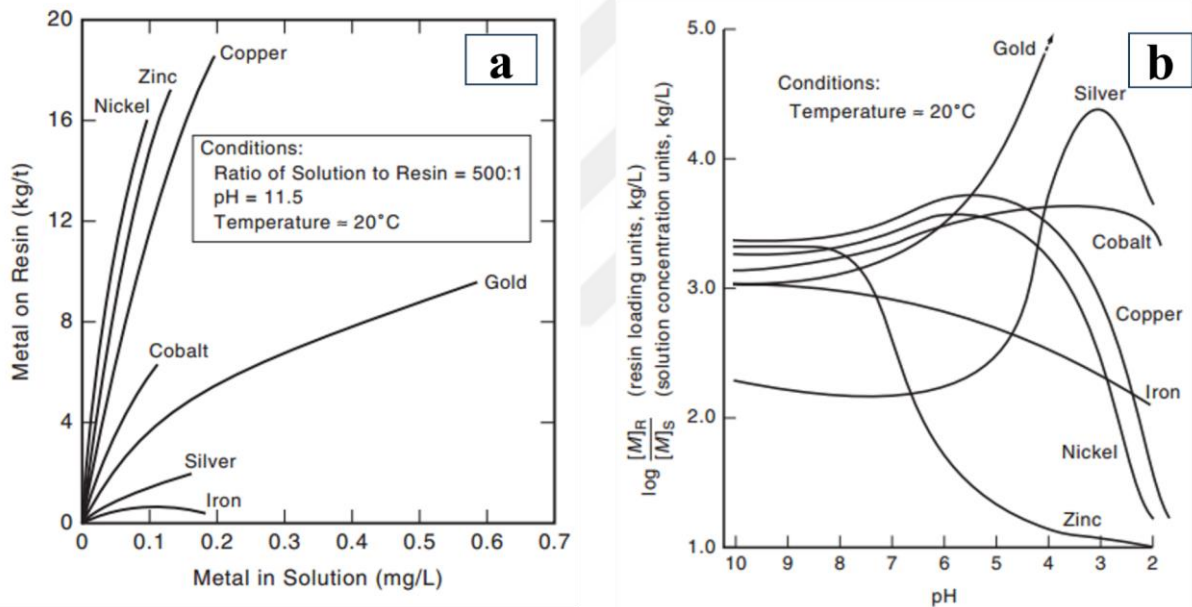
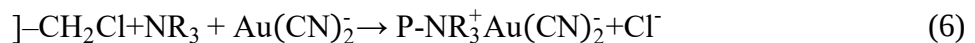
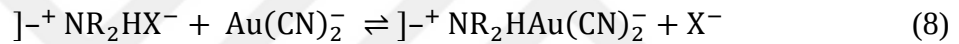


Figure 8. Equilibrium loading of various metal cyanide complexes (a) and the effect of pH on base metals loading onto strong base resin (b) (Marsden & House, 2006)

The adsorption mechanism of metals complexes onto the IX resin takes place through the reciprocation of the negatively charged counter ions on the active site of resin with the anionic complexes of the solution, Equation (6) shows the adsorption mechanism of aurocyanate complex on the strong-base resin (Adams, 2005).



Weak-base resins are a type of resins that possess primary, secondary, or tertiary functional groups, or a combination of these groups, on their surface (Marsden & House, 2006). Unlike strong-base resins, weak-base resins do not have a permanent charge on their surface. Therefore, before they can be utilized in the adsorption process, they need to undergo protonation process, as indicated by Equation (7). Once protonated, these resins become capable of exchanging ions, as demonstrated by Equation (8), which illustrates the ion exchange mechanism between weak-base resin and aurocyanate complex (Adams, 2005; Marsden & House, 2006). However, it is important to note that conventional weak-base resins are not sufficiently effective for gold hydrometallurgy (Adams, 2005). In contrast, Marsden and House (2006) have reported that weak-base resins modified with a small percentage of quaternary amine can be employed for the recovery of gold from cyanide PLS.



The capacity of the strong-base resin is approximately double that of the weak-base resin under the same adsorption conditions. This difference in capacity can be attributed to various factors, including the concentration of gold in the pregnant leach solution (PLS), the number of protonated active sites, the degree of protonation, and the resulting pH of the PLS. In contrast to weak base resins, the capacity of strong base resins remains unaffected by the pH of the solution, as depicted in Figure 8. This characteristic is considered a significant advancement in the application of strong base resins in hydrometallurgy, as highlighted by Marsden and House (2006).

The affinity of anionic complexes towards the active sites on the resin is influenced by various factors, including the properties of the functional group, the size and polarizability of the charge (Marsden & House, 2006). Also, the shape of the anion has less influence as Adams (2005). Conventional resins, despite their fast loading and high capacity, are known to be less selective and challenging to elute (Marsden & House, 2006). However, Harris. (1992) have contradicted this notion and reported the opposite. Generally, to enhance the selectivity of the resin, one can either reduce the density of active sites or increase the distance between functional groups using secondary and tertiary amines during the functionalization process. These principles have been applied in the design of gold selective resins like minix and AM2B (Adams, 2005).

Activated carbon is currently the primary adsorbent used in gold hydrometallurgy. However, modern ion exchange resins have several advantages over activated carbon. One significant advantage is the simplicity of the elution process, which does not require high temperatures (Harris et al., 1992; Xu et al., 2017). Additionally, ion exchange resins exhibit high selectivity over organic complexes. Gold selective resins, in particular, have been found to be superior to activated carbon in recovering gold from preg-robbing, as well as in dealing with high base metal concentrations in pregnant leach solutions (PLS) (Xu, et al., 2017). Resins also offer more flexibility compared to activated carbon. They can be designed to have better gold selectivity and have low demands for water quality. Furthermore, resins have shown excellent durability, with some studies claiming that they can be used for more than three cycles without noticeable deterioration (Deng, et al., 2020). In contrast, although resins can be modified to meet industrial demands, it is generally more expensive than activated carbon stated (Van Deventer, 2014). However, when considering the losses of gold during the washing of fine activated carbon particles and the thermal reactivation process, resins prove to be more economically effective since they do not require thermal reactivation (Harris, et al., 1992; Xu, et al., 2017) .

Many researchers have preferred ion exchange resins over activated carbon due to their higher loading kinetics and capacity. Resins are also less sensitive to organic foulants, elevated temperatures, and fine particles that can coat activated carbon. Additionally, resins can be used in many systems as resin in pulp (RIP), resin in solution (RIS), and resin in leach (RIL), which provide alternatives to carbon in column (CIC), carbon in pulp (CIP), and carbon in leach (CIL) systems. All these advantages make ion exchange resins a promising alternative to activated carbon in gold hydrometallurgy especially with the increasing demand for metal that forces the industry towards using refractory mineral resources.

In a study conducted by Kwak, et al. (2010), the researchers aimed to assess the effectiveness and selectivity of various materials including IX resin (Amberjet™ 400), AC, and a chemically modified biosorbent called polyethyleneimine modified biomass (PEIB). The study measured the maximum capacities and gold purity achieved by each material. The results showed that the IX resin had a maximum capacity of 427.77 mg/g and a gold purity of 96.56%. The activated carbon exhibited a maximum capacity of 170.64 mg/g with a gold purity of 94.57%. On the other hand, the chemically modified biosorbent, PEIB, demonstrated a maximum capacity of 361.76 mg/g and a gold purity of 97.72%. These findings highlight the varying capacities and purities achieved by different materials,

providing valuable insights for potential applications in gold extraction and purification processes.

In a recent study conducted by Deng, et al. (2020), the researchers explored the impact of gold concentration and the ratios of $[\text{CN}^-]:[\text{Cu}]$ and $[\text{Gly}]:[\text{Cu}]$ on the recovery of gold from synthetic cyanide-starved glycine solution using a newly developed resin called IXOS-AuC. Throughout the experiment, the pH was maintained at a constant value of 10.5, and the adsorbent dosage at 6 g/l. Interestingly, the study found that the $[\text{CN}^-]:[\text{Cu}]$ and $[\text{Gly}]:[\text{Cu}]$ ratios had no significant effect on the recovery of gold. However, the concentration of gold in the solution had a significant positive impact on its recovery. Under the optimal experimental conditions, the IXOS-Au-C resin demonstrated remarkable selectivity for gold over copper. While Approximately 100% of the gold present in the solution was successfully recovered, the recovery of copper was about 5%.

The research on the removal of mercury from PLS using IX resin has not received much attention, particularly in the context of cyanide PLS. The literature on this topic is scarce, and there has been no study conducted on the removal of mercury from glycine PLS to the best of the researchers' knowledge. However, a study by Staker and Sandberg (1987) reported the use of various IX resins, including IRA-430, 900, 2IK, SMA-I, and SBR, to selectively recover Au, Ag, and Hg from cyanide PLS. These resins were found to be effective in removing Hg-cyanide complex from the solution. Another study conducted by Chiarle, et al. (2000) investigated the efficiency and kinetics of mercury adsorption onto Duolite GT-73 resin. The experiment focused on the influence of pH ranging from 2 to 7 and mercury concentration ranging from 10 to 280 ppm on the adsorption process. The experimental conditions included a temperature of 20 °C and an adsorbent dosage of 0.5 g/l. The findings revealed that the pH had a positive impact on the adsorption efficiency, primarily due to the competitive adsorption of H^+ ions on the resin. In contrast, the initial mercury concentration had a negative effect on the adsorption kinetics, as the reaction was controlled by intraparticle diffusion.

2.7.3. AmberSep 91419 Resin (MINIX)

It is a chelating resin possesses a tri-butylamine functional group and exhibits a macroporous structure that selectively binds to gold. These chelating resins demonstrate fast reaction rates, which contribute to the enhanced retrieval of gold, especially when dealing

with carbonaceous preg-robbing ores that tend to absorb gold and gold cyanide complexes. Additionally, the resin showcases remarkable mechanical stability, thereby minimizing the production of fine particles during processing and ultimately improving the efficiency of gold recovery by reducing losses of Au-loaded resin, further information as shown in A crosslinked resin with a divinylbenzene functional group, the macroporous gold-selective resin is highly sought after in the gold industry due to its exceptional operating capacity and flow rates. In addition to its unique characteristics of volume expansion between 50 and 70% for at least 10 to 15 minutes is also noteworthy as it aids in the classification and cleaning of the beads while minimizing flow resistance. Studies have been conducted to compare the adsorption of gold from waste rinse water in the semiconductor manufacturing industry. In those studies, the effectiveness of three different resins: non-ionic Amberlite XAD-7HP, strong base Bonlite BA304, and Purolite A-500 was examined. The results showed that Purolite A-500 was the most suitable resin, as it demonstrated a gold adsorption rate of 99.6% and a sorption capacity of 53.6 mg gold per mL of resin (Nguyen et al., 2010). Due to their effectiveness, out of a group of seven different resins, these two resins described above were deemed suitable for use in this work based on their superior quality.

It has been identified as having a strong attraction to the Au-cyanide complex among other resins. A study conducted by Fedyukevich, et al. (2015) aimed to address the issue of Preg-Robbing by utilizing various resins to minimize gold loss. The researchers found that MINIX was the most effective resin, with a higher affinity towards aurocyanate exceeds that of active carbon. The utilization of AmberSep 91419 (MINIX) by the Anglo Asian Mining company has proven to be effective in the recovery of gold from cyanide PLS that contains approximately 1-2 ppm of gold, along with high levels of copper exceeding 1000 ppm. The presence of such a significant amount of copper makes the use of AC impractical. Within a 24-hour period at the mining site, the resin loading will contain approximately 160 mg/l of gold, 120 mg/l of silver, and 230 mg/l of copper. The adsorption efficiencies for gold and silver are observed to be 70% and 15% respectively, while the adsorption of copper is negligible. It has been observed that the efficiency of resin adsorption can be negatively impacted by the presence of excessive flocculant in the feed solution, as well as the presence of fine solid particles, which may originate from either precipitated solution or fine ore particles carried over from heap leaching (Hedjazi & Monhemius, 2014).

2.7.4. Purolite A500Cplus Resin

A crosslinked resin with a divinylbenzene functional group, the macroporous gold-selective resin is highly sought after in the gold industry due to its exceptional operating capacity and flow rates. In addition to its unique characteristics of volume expansion between 50 and 70% for at least 10 to 15 minutes is also noteworthy as it aids in the classification and cleaning of the beads while minimizing flow resistance. Studies have been conducted to compare the adsorption of gold from waste rinse water in the semiconductor manufacturing industry. In those studies, the effectiveness of three different resins: non-ionic Amberlite XAD-7HP, strong base Bonlite BA304, and Purolite A-500 was examined. The results showed that Purolite A-500 was the most suitable resin, as it demonstrated a gold adsorption rate of 99.6% and a sorption capacity of 53.6 mg gold per mL of resin (Nguyen et al., 2010). Due to their effectiveness, out of a group of seven different resins, these two resins described above were deemed suitable for use in this work based on their superior quality.

2.7.5. Adsorption Kinetics Models

Adsorption kinetics is very important to develop adsorption systems (Ho & McKay, 1999); since it can describe the rate at which the solute is adsorbed onto the surface, it can be described using many different models, among those models Pseudo-first order (PFO) and Pseudo-second order (PSO) models were the most used in the last two decades. Both models can be driven from Langmuir hybrid expression, Equation (9).

$$\frac{dq_t}{dt} = K_1(q_e - q_t) + K_2(q_e - q_t)^2 \quad (9)$$

The Pseudo-first order (PFO) model is derived from the Langmuir hybrid equation by assuming that the rate of adsorption is proportional to the difference between the equilibrium adsorption capacity (q_e) and the adsorption capacity at any given time (q_t). This assumption leads to a first-order rate equation, which can be integrated to obtain an expression for the amount of solute adsorbed as a function of time. In the case of $q_e \ll K_1/K_2$ pseudo-first order model becomes the most suitable for the adsorption system, it is generally expressed in the form of what so called Lagergren's first order rate expression, Equation (10)

(Revellame et al., 2020). The integration of this equation in the boundaries condition of $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives Ho and McKay (1999)'s linearized form of PFO, Equation (11).

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (10)$$

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \quad (11)$$

The PFO is linked to two primary issues: the model's discontinuity once equilibrium is achieved and the need to assume a value for q_e in order to calculate the other model parameters. These factors have led many researchers to prefer using PSO more, particularly after the study conducted by Ho and McKay in 1999 (Revellame et al., 2020). The PSO model is also derived from the Langmuir hybrid equation, where it assumes that the rate of adsorption is proportional to the square of the difference between q_e and q_t . This assumption results in a second-order rate equation, which can be integrated to derive an expression for solute adsorbed over time. In cases where $q_e \ll K_1/K_2$ the Langmuir equation is simplified to the integrated PSO form, Equation(12). which is generally used in the linearized form of driven by Ho and McKay (1999), Equation (13).

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \quad (12)$$

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{K_2 q_e^2} \quad (13)$$

The adsorption rate of a specific substance can be described by the PFO and PFO. However, these parameters do not provide any information regarding the limiting step of the adsorption process. In order to determine the limiting step, the intraparticle diffusion model (IPDM) is generally employed and fitted to the experimental data. Equation (14) represents the mathematical description of this model. The value of K_{id} can be derived from the slope of the plot of q_t against $t^{0.5}$. If the plotted data exhibits a linear regression, it indicates that the IPDM is the limiting step. Conversely, if the adsorption process undergoes multiple steps before reaching equilibrium, it suggests that the adsorption does not solely rely on the IPDM.

$$q_t = K_{id}t^{0.5} \quad (14)$$

2.7.6. Adsorption Isotherms

The comprehension of the adsorption mechanism holds immense importance in the design of ADR systems (Guo & Wang, 2019; Wang & Guo, 2020). There are several approaches to determine this mechanism, with the characterization of adsorbents before and after the adsorption process and the plotting of adsorption equilibrium information being the most employed methods. Among these methods, plotting the adsorption data is particularly popular due to its simplicity and ability to provide insights into the maximum capacity of the adsorbent (Wang & Guo, 2020).. Various adsorption isotherm models, such as Freundlich, Langmuir, and Temkin, are utilized in this field (Guo & Wang, 2019; Wang & Guo, 2020). However, Langmuir and Freundlich's models are the most widely used for interpreting and understanding the adsorption mechanism.

Initially developed to describe solid-gas systems, the Langmuir adsorption isotherm was later adapted for solid-liquid systems (Wang & Guo, 2020). This model assumes a homogeneous surface of the adsorbent and monolayer adsorption (Guo & Wang, 2019). The nonlinear and linear models are represented by Equations (15) and (16), respectively.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (15)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (16)$$

The estimation of parameters q_m and K_L can be achieved by plotting the values of C_e and q_e for the nonlinear equation, and C_e/q_e against C_e for the linear equation. The linear equation offers a simpler approach for estimating these parameters compared to the nonlinear equation (Guo & Wang, 2019), However, it is important to note that the it may result in less accurate estimations (Wang & Guo, 2020). Furthermore, there exist four distinct methods for fitting the linear equation, and each method yields different estimations for the parameters. Among these methods, Equation (16) demonstrates superior performance when compared to the other linear fitting equations (Guo & Wang, 2019).

Once the parameters have been established, the characterization of adsorption behaviour based on the Langmuir isotherm model can be determined using the separation factor R_L , Equation (17). The adsorption process can be classified as linear, irreversible, unfavourable, or favourable depending on the values of R_L . Specifically, when ($R_L = 1$) the adsorption is considered linear, when ($R_L = 0$) the adsorption is irreversible, when ($R_L > 1$) the adsorption is unfavourable and ($0 < R_L < 1$) the adsorption is favourable (Al-Ghouti & Da'ana, 2020).

$$R_L = \frac{1}{1 + K_L C_o} \quad (17)$$

Freundlich, the oldest known adsorption isotherm model, has been widely employed to empirically represent adsorption from diluted solutions (Malarvizhi & Ho, 2010). This model is particularly suitable for describing non-ideal, multilayered reversible adsorption systems. It incorporates the notion of equal distribution of active sites and their energies on the adsorbent, without requiring the surface of the adsorbent to be homogeneous (Al-Ghouti & Da'ana, 2020). Wang and Guo (2020) also suggest that this model can effectively describe chemical adsorption with a surface coverage fraction of approximately 50%. Moreover, the Freundlich model can be applied in both linear and non-linear forms, as represented by Equation (18) and (19), respectively.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (18)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (19)$$

K_F and $1/n$ represent constants that can be determined through the linearized form by graphing the $\log q_e$ vs. $\log C_e$. The slope of the line corresponds to the value of $1/n$ while the intercept represents K_F . On the other hand, the values K_F and $1/n$ of obtained from the non-linearized equation can be obtained by plotting C_e Vs q_e (Wang & Guo, 2020).

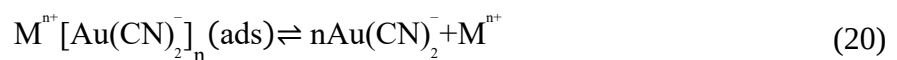
2.8. Gold and Mercury Elution

Elution, also known as desorption or stripping, is the reverse process of adsorption. Its purpose is to generate a smaller volume of high-quality gold solution that is suitable for final gold recovery through electrowinning or zinc precipitation. Elution is the complete opposite of adsorption, as it involves reversing the conditions under which adsorption occurs (Marsden & House, 2006). This process plays a vital role in the gold industry and is considered the primary reason for the widespread industrialization of AC adsorption in gold processing plants. Although AC adsorption was discovered in the mid-19th century, the application of AC techniques such as carbon-in-pulp (CIP) was not possible until the discovery of AC elution in 1952. Prior to that, gold recovery from AC was achieved through incineration (Van der Merwe, 1991).

Since the development of the first AC elution method, various other elution processes have been developed, taking advantage of the affinity of AC and ion exchange (IX) resin to certain chemicals. Some of these methods are conducted in a basic environment, while others utilize acidic eluents. Additionally, certain elution methods have been found to be selective and highly applicable in gold hydrometallurgy, while others require further development.

2.9. Activated Carbon Elution Methods

The loaded AC is eluted to send the valuable metals to the downstream process and recycle the AC. The desorption mechanism of gold from AC can be simply represented by Equation(20). But the exact mechanism is more complicated as so the adsorption (Marsden & House, 2006).



The elution process is influenced by various factors, including temperature, cyanide concentration, ionic strength, pH, the presence of other metal-cyanide complexes and ions, and the use of organic solvents in the eluent. Among these factors, temperature, pH, and cyanide concentration have a positive effect on the elution process. For instance, Marsden and House (2006) demonstrated that increasing temperature enhances the elution of gold from AC. Since the adsorption of gold onto AC is exothermic, higher temperatures significantly improve the elution rate as it is shown in Figure 9. In fact, the elution rate of

Au at 180 °C is eight times faster than at 90 °C. Temperature is considered the most crucial factor in gold elution from AC, according to Van der Merwe (1991).

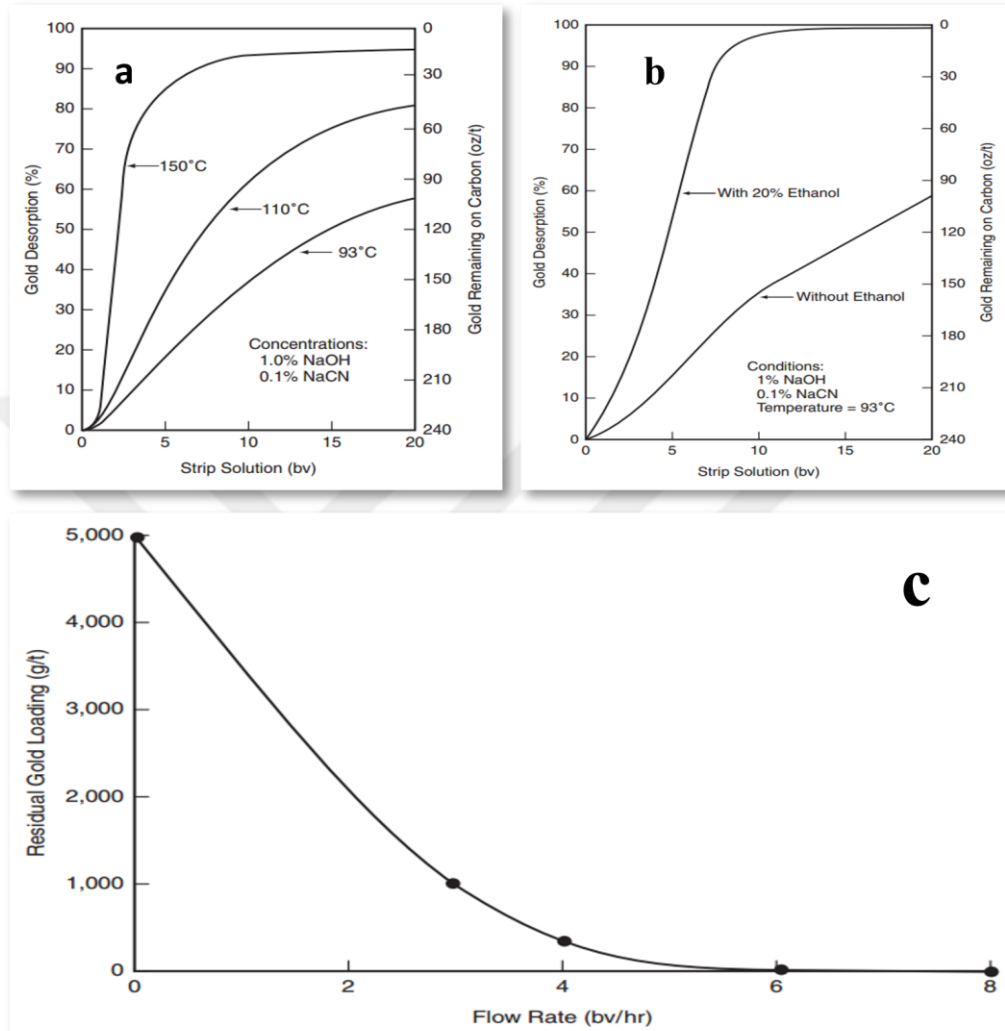


Figure 9. Effect of temperature (a), organic solvent addition (b), and the eluant flow rate (BV/hr) on the elution of aurocyanide from AC (Marsden and House, 2006)

On the other hand, the gold concentration and ionic strength of the solution have an inverse effect on elution. Lowering the ionic strength has a more significant impact on elution than cyanide concentration itself. Additionally, the addition of organic solvents can enhance the elution process by increasing the activity of certain ionic species, such as CN^- . This results in an increased elution rate, as depicted in Figure 9. However, organic solvents alone are not sufficient to elute gold in the absence of cyanide (Van der Merwe, 1991; Van Deventer & Van der Merwe 1994).

Furthermore, the flow rate of the eluant plays a crucial role in the elution rate, as shown in Figure 9. A higher eluant flow rate leads to a faster elution rate. Overall, the influence of these factors can be ranked as follows: temperature > cyanide and hydroxide concentrations > the ionic strength of the eluant, according to Van der Merwe (1991) and Van Deventer (1994). These factors collectively determine the efficiency and effectiveness of the elution process in extracting gold from activated carbon. Various elution techniques have been devised, taking into account the variables that influence the process. Among the well-known methods are Zadra, Anglo American Research Laboratories (AARL), and organic solvent-assisted methods, which are modifications of the former two techniques, incorporating the use of organic solvents.

2.9.1. Zadra Elution Process

The Zadra elution process involves the recycling of a sodium hydroxide solution with a concentration of 1% w/v and a sodium cyanide solution with a concentration of 0.2% w/v through a bed of loaded AC at a temperature range of 95-100 °C for approximately 72 hours under atmospheric pressure. However, the process has been recently modified to be conducted under elevated temperature and pressure, resulting in a reduced elution time of 10-12 hours (Beyuo & Abaka-Wood, 2016). The pressure is typically maintained between 400-500 Kpa, the temperature is set at 140 °C, and the flow rate is around 2 BV/h. In some cases, the elution time can be further reduced to 8 hours (Marsden & House, 2006). The process does not require cyanide pretreatment, and the eluant is recycled in a closed circuit with electro-winning cells and the column (Van der Merwe, 1991). Researchers have achieved elution of over 90%, 78%, and 76% for gold, silver, and mercury, respectively, using 16 BV of an eluant containing 2% w/v sodium hydroxide and 2% w/v sodium cyanide. However, achieving selective mercury elution is challenging, and the mercury that is later eluted in conjunction with gold can contaminate the equipment and the atmosphere of the processes that follow the elution process (Adams, 2005; Bunney et al., 2010). Although mercury can be removed from AC using nitric acid (Marsden & House, 2006), a complete elution is difficult to achieve. The Jerritt Canyon plant in Nevada has achieved a mercury removal efficiency of about 60% by applying an intensive acid washing solution containing 20 - 30% nitric acid for about two hours at a temperature of 80 °C (Adams, 2016).

2.9.2. Anglo American Research Laboratories (AARL) Elution Process

The AARL process involves several steps. Initially, the loaded AC is washed with 1 BV diluted HCl to remove salts such as CaCO_3 , followed by water washing using 2 - 4 BV water. The carbon is then pre-soaked in a pretreatment solution containing 3% NaCN solution and 1-2% NaOH for approximately 30 minutes. Elution is carried out using 5 - 8 BV of highly softened water at a flow rate of 2 BV/hr (Van der Merwe, 1991; Marsden & House, 2006), with the water temperature ranging from 110 – 120 °C and pressure between 70 - 100 kPa. The sodium content in deionized water should be below 300 ppm (Van der Merwe, 1991). This process can elute more than 90% of gold, with the elution profile listed as mercury, silver, and gold. However, mercury has the sharpest elution profile but the lowest overall recovery of (40-50)% (Bunney et al., 2010).

To address the issue of mercury elution, a hybrid of two-stage elution methods can be used. This method involves the use of 11 BV of 2% w/v sodium hydroxide and 5% w/v sodium cyanide at 90 °C in the first stage, followed by soaking in the same eluate at 130 °C and then elution by 6 BV of distilled water. This method can elute a total of 100% of the mercury in the first stage, and a total of 94% and 85% of gold and silver, respectively, with silver showing less selectivity (Bunney et al., 2010).

2.9.3. Organic Solvent-Assisted Elution

The acceleration of elution in organic solvent-assisted methods has been extensively documented using alcohols and glycols. It has been found that employing 20-25% ethanol or methanol at atmospheric conditions and low temperatures (~95 °C) can significantly reduce the elution time to 12-16 hours (Marsden & House, 2006). According to Van der Merwe (1991), it was reported that the effectiveness of organic solvents in facilitating gold elution can be ranked as follows: acetonitrile > methyl ethyl ketone > acetone > dimethyl formamide > ethanol. Marsden and House (2006) further emphasized that alcohol is highly efficient compared to other organic solvents. However, due to their high flammability, glycols are sometimes used as a safer alternative, albeit with reduced effectiveness.

The solvent distillation process is an alternative method for elution. This process involves configuring the column with a heater at the bottom and a condenser at the top. Prior to elution, the loaded AC is pre-soaked with a solution containing 1-2% NaOH and 5-10% NaCN at ambient temperature. Elution is then carried out using ethanol, methanol, or

acetonitrile (Marsden & House, 2006). During this process, the loaded AC in the column acts as a fractionating medium, with the organic solvent condensing at the top of the column and washing the gold as it moves to the bottom (Van der Merwe, 1991). This process is relatively quick, taking an average of 8 hours, and has several advantages, including the ability to operate at a low temperature of 65-80 °C compared to other methods (Marsden & House, 2006), and the use of a small volume of solution, approximately 1 BV, which results in a highly concentrated solution. However, this process is not recommended when the carbon amount is large (Van der Merwe, 1991).

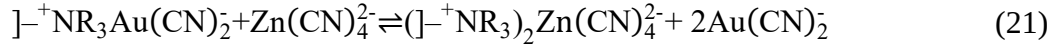
2.10. Ion Exchange Resin Elution Methods

Adams (2016) has noted that IX resin active sites exhibit distinct characteristics from AC. As a result, different elution procedures are required, as highlighted by Marsden and House (2006). The literature has established that weak base resin can be easily eluted using sodium hydroxide, while zinc cyanide, ammonium thiocyanate, and acidic thiourea are commonly used for strong base resins elution (Adams, 2016). Additionally, Staker and Sandberg (1987) have patented a chloride and hydroxide salts mixture as an elution method. Each of these methods has its own advantages and disadvantages and can be employed to elute specific types of resins.

2.10.1. Elution of Strong-Base Resins

As previously mentioned, the elution process from this particular type of resin is challenging due to the high ion strength. There are two possible methods for achieving elution. One approach involves introducing a high concentration of competing anions, such as thiocyanate, chloride, bisulphate, nitrate, or cyanide ions, into the system. Alternatively, a complexing anion like Zn-cyanide, which exhibits a stronger affinity for resins compared to gold complex, can be utilized to disrupt the adsorption equilibrium (Marsden & House, 2006).

The elution of gold from the strong base resin can be achieved using a solution containing 0.5 M zinc cyanide can be employed at a temperature ranging from 60 to 50 °C (Marsden & House, 2006). This elution process is applicable to all types of nonselective strong-base resins. The Equation (21) illustrates the mechanism of this elution process (Adams, 2016).

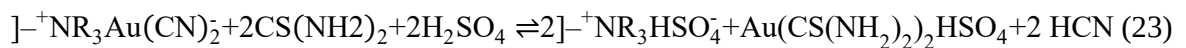


Despite its advantages in terms of safety and equipment protection due to its occurrence in a basic medium, the process discussed in this text also has several disadvantages (Marsden & House, 2006). One major drawback is the reversibility of the reaction, as indicated in Equation (21). This necessitates either maintaining a minimal gold concentration in the eluant through electroelution or using a large amount of eluant to ensure efficient gold deposition on the cathodes (Adams, 2016). Furthermore, compared to other elution methods, this process is notably slow. Additionally, the resin used in the process exhibits a high affinity for zinc cyanide, requiring the elution of loaded zinc cyanide and reactivation of the resin using sulfuric acid or another mineral acid, as shown in Equation (22). The regeneration process itself is considered a drawback, as it produces hydrocyanic acid gas, which must be contained in a solution of sodium or potassium hydroxide and recycled in either a leaching or elution process (Fleming & Cromberge, 1984).



In 1984, Fleming and Cromberge conducted a study to evaluate the elution of gold cyanide complex from a strong base resin IRA 400UC. The study aimed to determine the impact of various factors, including the concentration of zinc cyanide $\text{Zn}(\text{CN})_4^{2-}$, temperature, electrowinning cell current, and eluate flow rate, on the efficiency of elution. The researchers found that the highest elution efficiencies were achieved when the zinc cyanide concentration was 0.46 M, the temperature was 20 °C, the cell current was 1 A, and the eluate flow rate was 14 l/h (Fleming & Cromberge, 1984).

The elution process of gold from strong resin using thiourea is based on the formation of a cationic complex between thiourea and adsorbed gold. This complex can be easily washed away by water, the mechanism is presented by Equation **Error! Reference source not found.** (Marsden & House, 2006).



The concentration of thiourea and sulfuric acid positively affects the process, and increasing the temperature can also have a positive impact since the activation energy of the

reaction is estimated to be 19 kJ/mol (Fleming & Cromberge, 1984). However, it should be noted that increasing the temperature leads to increased consumption of thiourea, as it decomposes at ambient temperature in an acidic environment (Marsden & House, 2006). Previous studies have shown that using an eluant containing 1M thiourea and 0.5M sulfuric acid at 60°C can effectively elute the resin Adams (2016). These findings are consistent with the research conducted by Fleming and Cromberge (1984), who investigated the effect of various factors on the elution of aurocyanide complex from IRA 400UC resin. They found that the most suitable conditions for elution were a concentration of 1M thiourea and 2M sulfuric acid, a temperature of 20°C, a cell current of 2A, and an eluate flow rate of 10 l/h. Additionally, they observed that increasing the temperature could reduce the elution time to 6 hours. The cell current and flow rate of eluate recirculation were found to have a negligible effect on the elution rate due to the irreversibility of the reaction.

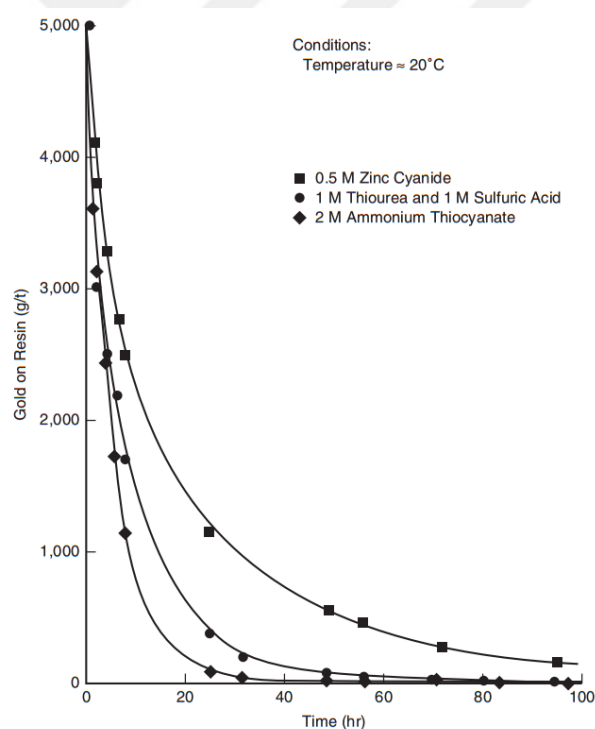


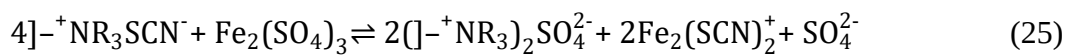
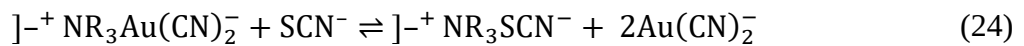
Figure 10. Elution rate of gold from a strong base resin using different eluents (Marsden & House, 2006)

Despite its cost-effectiveness and popularity among Russian metallurgists, the process has several drawbacks, as noted by Fleming and Cromberge (1984). These include the high corrosion of electrodes, high reagent consumption in acidic media, and shortened resin lifespan due to osmotic shock caused by the differing conditions of adsorption and elution

(Marsden & House, 2006). Nonetheless, the process remains widely used in laboratory, pilot, and full-scale applications (Fleming & Cromberge, 1984).

Equation (24) demonstrates that thiocyanate can displace adsorbed gold from strong base resins. By utilizing a solution containing approximately 2M of thiocyanate at a pH level of 7-8, elution rates higher than those of zinc cyanide and thiourea can be achieved, as depicted in Figure 10 (Marsden & House, 2006). Remarkably, an efficiency of 99% can be attained within a mere 6 hours (Fleming & Cromberge, 1984). Although the process exhibits a positive response to elevated temperatures, satisfactory rates can still be obtained under moderate temperature conditions, thanks to the low activation energy of the reaction (Fleming & Cromberge, 1984; Marsden & House, 2006).

In a study done by Fleming and Cromberge (1984), the effect of thiocyanate concentration, the pH, the eluent temperature, current of the cell, and the eluate flowrate on the elution efficiency were investigated. The elution was found to be affected positively linearly by the increase of thiocyanate concentration, cell current and eluate flowrate, the optimums were 2M, 1A and 10 l/h respectively. In the case of pH, the best desorption rate was achieved at a nearly moderate pH of 7-8. Although increasing the temperature led to an increase in elution rate, the rates obtained at normal temperature are still satisfying (Fleming & Cromberge 1984).



Compared to the thiourea elution method, the use of thiocyanate has several advantages. It is less corrosive and less toxic, as reported by Marsden and House (2006). However, the use of thiocyanate is less cost-effective due to the need to reactivate the resin after elution and wash the large amount of thiocyanate that has been adsorbed onto the resin, as noted by Fleming and Cromberge (1984). The resin must be regenerated not only to restore its capacity but also to recycle the significant amount of thiocyanate that was adsorbed onto it. To achieve this, mineral acids or complex metal ions were suggested as regeneration mechanisms. However, the use of mineral acids was not successful due to the rapid decomposition of thiocyanate in acidic media. Therefore, the use of Fe^{3+} to form a

cationic complex with thiocyanate, as shown in Equation (25), is applied (Fleming & Cromberge, 1984; Marsden & House, 2006).

The utilization of chloride ions as an eluent for gold, mercury and silver has been documented by Marsden and House (2006). However, Staker and Sandberg (1987) have indicated that an oxidant, such as NaOCl, is necessary for the elution of gold cyanide radioisotopes. Marsden and House (2006) found that the elution of mercury was achieved using 2 N hydrochloric acid, while the elution of silver required a solution containing 200 g/l sodium chloride in 1 N hydrochloric acid. Building upon this information, Staker and Sandberg (1987) developed a sequential elution method for gold, silver, and mercury cyanide radioisotopes using five different types of strong base ion exchange resins. By employing 40 bed volumes of 2N H₂SO₄, 200 g/l of sodium chloride in 1N HCl, and a mixture of 0.75% NaOCl, 150 g/l NaCl, and 5 g/l NaOH, selective elution of 100% of mercury and silver, as well as 93-88% of gold were achieved.

Mercury contamination in PLS is a significant concern due to its toxicity and potential environmental impact. PLS is a solution that is generated during the leaching process of ores, typically containing valuable metals such as gold or silver. However, it can also contain various impurities, including mercury, which need to be removed before further processing. The research on the removal of mercury from PLS using IX resin has not received much attention, particularly in the context of cyanide PLS where literature on this topic is scarce. Additionally, there has been no study conducted on the removal of mercury from glycine PLS to the best of the researchers' knowledge. Therefore, there is a clear need for further investigation and research into the elimination of mercury from PLS, particularly in the context of cyanide and glycine PLS. This research could contribute to the development of more efficient and sustainable methods for mercury removal, ensuring the protection of the environment and human health in mining operations.

2.10.2. Elution of Weak-Base Resin

The elution of weak base resin can be achieved using the same methods as strong base resin elution, but there is also another more efficient method available. When the resin is exposed to high alkaline conditions, it loses its ion exchange properties and becomes free base resin (Fleming & Cromberge, 1984). Taking advantage of this fact, weak base resin can

be easily eluted by using a sodium hydroxide solution, as shown in Equation (26) (Marsden & House, 2006).

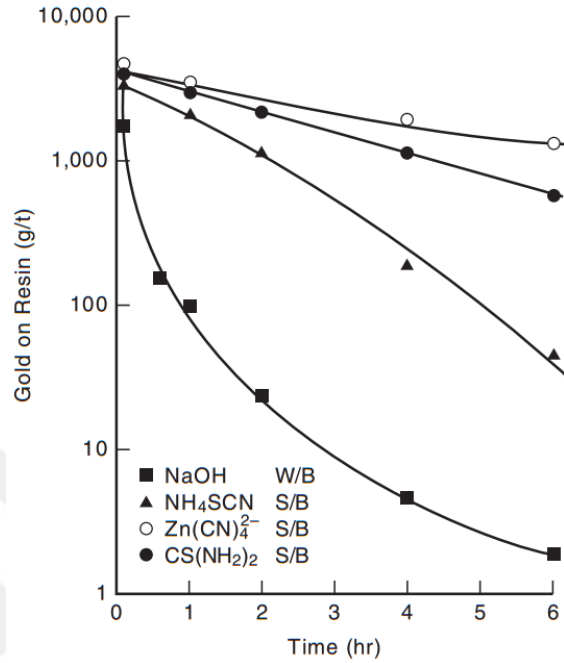


Figure 11. Difference in the elution rates between strong base and weak base resins (Marsden & House, 2006).

The rate at which elution occurs depends on the concentration of sodium hydroxide and the temperature. It has been reported that the effect of sodium hydroxide is positive up to a concentration of 0.5 M. However, increasing the concentration beyond this point has a negative impact on elution. This could be due to the increase in viscosity of the eluant, which leads to a decrease in the mass transfer rate, or the physical entrapment of gold by metal hydroxides (Fleming & Cromberge, 1984).



While the elution rate is positively influenced by temperature, even at ambient temperature, the elution rate for weak base resin is still higher compared to that of activated carbon and strong base resins, as depicted in Figure 11.

2.11. Justifications of the Thesis

The previous discussion on the gold artisanal mining industry has clearly highlighted that despite the sanctions imposed by the Minamata convention on the use of mercury, the industry continues to thrive. Currently, this industry is practiced in more than 70 countries and serves as a source of income for over 100 million individuals. However, its inefficiency leads to the accumulation of millions of tons of tailings containing significant amounts of mercury, posing a severe environmental threat as these levels continue to rise. Additionally, these tailings also contain a considerable amount of gold, making them an economically attractive source for both large- and small-scale mining companies.

To extract gold from these tailings, companies rely on the cyanidation process, which is the dominant method in the gold mining industry. However, this process has adverse health and environmental impacts and is inefficient when applied to certain refractory ores. Furthermore, the Minamata convention prohibits the use of cyanidation to leach gold from mercury-containing ores and secondary source materials like ASGM tailings. Despite this prohibition, companies continue to process these tailings using cyanide due to the lack of viable alternatives.

As a result, alternative methods have been explored to recover gold from tailings. In recent years, the use of amino acids, specifically the glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) and potassium permanganate (KMnO_4) system, has been investigated. This green and innovative alternative method has shown promise. Furthermore, a patented process utilizing the same system has been developed for ores and ASGM tailings containing mercury. This new process shows great promise as it can compete with cyanidation in terms of efficiency and operation cost. However, downstream processes such as adsorption, desorption, and recovery (ADR) are still lacking, making it a rich topic for further research.

Considering this, the present thesis aims to undertake a comprehensive and pioneering study on the adsorption and selective elution of gold, mercury, and other precious metals using ion exchange resins and activated materials. This study holds significant global implications, particularly in the realm of green mining. By paving the way for the industrialization of this technology, it aligns with the international drive towards sustainable mining practices. Moreover, it contributes valuable insights to the scientific community, enhancing our understanding of the behaviour of gold and mercury-glycine complexes. Additionally, this research enables the exploitation of mercury-bearing gold ores, thereby

stimulating economic growth through the creation of new markets. Furthermore, it is worth highlighting the substantial environmental benefits of this study, as it addresses the issue of mercury contamination in ASGM tailings, thus promoting cleaner and safer mining practices.



3. MATERIAL AND METHODS

3.1. Introduction

The main focus of this thesis was to study the selective recovery of gold and mercury from a glycine pregnant solution using IX resin and AC. However, instead of examining the leaching process of the sample itself, the study utilized the optimal conditions established in previous glycine leaching studies conducted on a similar sample from Sudan to generate a leaching solution for the experiments. The sample used in this study was obtained from the Kombo Laka Artisanal mining region in Cameroon, which is located approximately 490 km northeast of the capital Yaoundé and 51 km west of the Meiganga district. Before conducting leaching and recovery experiments, the sample underwent a detailed characterization through chemical, mineralogical, and sieve analysis.

To minimize the amount of sample used, a series of experiments were conducted on a synthetic solution using the response surface central composite design (CCD) methodology. Once the optimal conditions of adsorption were determined, the selective elution of these metals was also investigated on IX resins and AC loaded with a synthetic solution. This investigation aimed to identify the best parameters for a final test on an original solution derived from the ASGM tailing sample.

3.2. Materials

The thesis incorporates two distinct sections for the materials utilized. The initial segment encompasses the chemical materials that were employed throughout the various stages of the thesis, ranging from characterization to analysis. Also, it contains the detailed information about the adsorbents used in the thesis. The second segment is exclusively dedicated to the instruments employed throughout all the steps of the thesis.

3.2.1. Chemical Materials

All the chemical materials utilized in this thesis as listed in Table 2 were procured exclusively from certified and globally acknowledged suppliers. While certain materials were employed in their original form, others were occasionally diluted or combined with

Table 2. Chemical materials used within the scope of this study.

Name	Form	MW g/mol	Comp.	Assay%	The objective
Hydrochloric acid	HCl	36,46	Isolab	37%	pH adjustment, dilution of samples
Nitric acid	HNO ₃	63,01	Isolab	≥65%	dilution of samples
Hydrofluoric acid	HF	20.01	Isolab	40%	Sample digestion
Sulfuric acid	H ₂ SO ₄	98.08	Merck	95 - 98%	Mercury elution
Sodium hydroxide	NaOH	40	Isolab	99 %	pH adjustment and solution PREP
Sodium boron hydride	NaBH ₄	37,83	Kimetan	-	Reducing agent for mercury
Sodium cyanide	NaCN	49,01	Merck	≥ 95 %	For gold leaching
Sodium Chloride	NaCl	-	Merck	-	Au & Ag elution
Sodium Hypochlorite	NaClO	-	Merck	-	Au & Ag elution
Sodium perchlorate	NaClO ₄	-	Merck	-	Au & Ag elution
Silver nitrate	AgNO ₃	169,87	Sigma Aldrich	>99.5%	Free cyanide titration
Gold standard	Au	-	Merck	1000 mg/L	synthetic solution, AAS calibration
Silver standard	Ag	-	Merck	1000 mg/L	synthetic solution, AAS calibration
Mercury standard	Hg	-	Merck	1000 mg/L	synthetic solution, FIAS calibration
Copper standard	Cu	-	Merck	1000 mg/L	synthetic solution, AAS calibration
Glycine	C ₂ H ₅ NO ₂	75.07	Merck	-	Leaching, synthetic solution
Potassium Permanganate	KMnO ₄	-	Merck	-	Leaching, synthetic solution

additional substances to align with the intended application. It is noteworthy that all the materials employed in this research were stored under the recommended optimal conditions. Furthermore, specific prepared standards and synthetic solutions were carefully preserved to ensure their viability during the testing phase.

3.2.2. Adsorbents Used in the Thesis

Throughout this thesis, three different adsorbents were used. Included IX resins and activated carbon. Two different IX resins were used in this work namely AmberSep™ 91419 and PuroliteA500Cplus. Their chemical and physical properties, and characteristic are presented in Table 4. The activated carbon utilized in this research, namely MFCARB GC E612, was derived from coconut shells and functions, particularly in gold recovery. Two primary agents employed for activation include air and steam. Table 3 shows the main technical information required for activation carbon selection.

Table 3. Characteristics of the activated carbon

Parameter	Unit	Specification	Test Method
Moisture	%	3 max.	ASTM D2867
CTC Adsorption	%	60 min	ASTM D3467
Apparent density	Kg/m ³	480 -530	ASTM D2854
Ash Content	%	3 max.	ASTM D2866
Iodine	mg/gm	1100	ASTM D4607
pH	-	9-11	ASTM D3838
Ball Pan Hardness	%	99 min	ASTM D3802
Platelets	%	3% max	AARL
Attrition	%	2 % max	AARL
K value	%	29 kg/ton	AARL
BET Surface Area	m ² /g	903.31	-
Mean particle size	mm	2.48	-

Table 4. Physical and chemical properties, and the operating conditions of the resins.

Physical Properties		
	AmberSep™ 91419	PuroliteA500CPlus
Copolymer	Styrene-divinylbenzene	polystyrene - divinylbenzene
Matrix	Macroporous	Macroporous
Type	Chelant	Crosslinked
Functional Group	QA (t-butylamine)	QAm
Physical Form	White to tan, hard, opaque, spherical beads	White to Bayj, hard, opaque, spherical beads Spherical Beads
Particle Density	1.08 g/mL	1.08 g/mL
Chemical Properties		
Total Capacity	0.23 – 0.33 eq/L	1.1 eq/L
Dry Weight Capacity	0.8 – 1.2 meq/g	-
Water Retention	49 – 59%	54 - 65 %
Particle Size		
Particle Diameter	760 – 1200 µm	425 - 1200 µm
Fine Beads	$< 768 \mu\text{m} \leq 5\%$	$< 425 \mu\text{m} \leq 2 \%$
Coarse Beads	$> 1190 \mu\text{m} \leq 2\%$	-
Suggested Operating Condition		
Maximum Operation Temperature	OH ⁻ form 60°C/ Cl ⁻ form 100°C	OH ⁻ form 60°C/ Cl ⁻ form 100°C
pH Range	0 – 14	0 – 14
Bed Depth, min.	800 mm (2.6 ft)	-
Total Rinse	2 – 4 BV	-
Regenerant	Thiourea acidified	-

3.2.3. Instruments

In order to ensure the proper execution of the research, a variety of instruments were required. Table 5 shows the details of the used instruments. Several of these instruments were located within the department of Mining Engineering, while others were housed in the central laboratory of the University. Additionally, certain instruments were available in certified laboratories. The characterization process involved the utilization of various instruments such as XRD, SEM, SEM EDX, FTIR, and TG to analyse the samples and adsorbents. For the adsorption experiments, a sensitive balance, magnetic shaker, orbital shaker, centrifugal separator, and pH meter were employed. To analyse the results obtained from the experiments, ICP, AAS, and FIAS were utilized.

Table 5. Different instruments used in within the scoop of this project.

Instrument	Model
Atomic Absorption Spectrometer (AAS)	Perkin Elmer/ AAS AAnalst 400
FIAS	Perkin Elmer/ AAS AAnalst 100
Orbital Shaker	Wiggen Hauser
pH Meter	Hanna /HI 2211 pH/ORP Mete
Magnetic Stirrer	SH-5 Heating Stirrer
X-Ray Diffractometer (XRD)	PANanalytical X'Pert3 powder
Cold Steam Technique	Perkin Elmer/FIAS100
Scales	Precisa XT 6200C
Centrifugal liquid solid separator	NF400
Mechanical Mixer	IKA RW 20 digital
Polarizing Ore microscope	Clemex
Oven	VentiCell
Fourier-transform infrared spectroscopy (FTIR)	IRSpirit - SHIMAZDU
Scan Electron Microscopy (SEM)	JSM-6610

3.3. Sample Preparation

The weighing about 13.5 kg was sourced from artisanal mining tailing dam in Cameroon. In order to obtain two equally representative samples, the original sample was riffled. One of the samples was stored in a zipped plastic bag, while the other was divided into sub-samples of about 870 grams using a rotary sample divider (Fritsch 27). Due to its coarse nature, the sample was ground to a size of -150 microns in a laboratory rod mill with a diameter of 19.5 cm. The grinding process lasted for 18 minutes at a speed of 42 rpm, which corresponds to 67.7% of the critical speed (62 rpm).

3.4. Sample Characterization

In order to analyse the particle size distribution of the given sample, a wet sieve analysis was performed using a range of sieves from 1400 to 38 μ m. A specific quantity of 880 g was sieved, and to eliminate any particles that were stuck, the sieves underwent an ultrasonic bath.

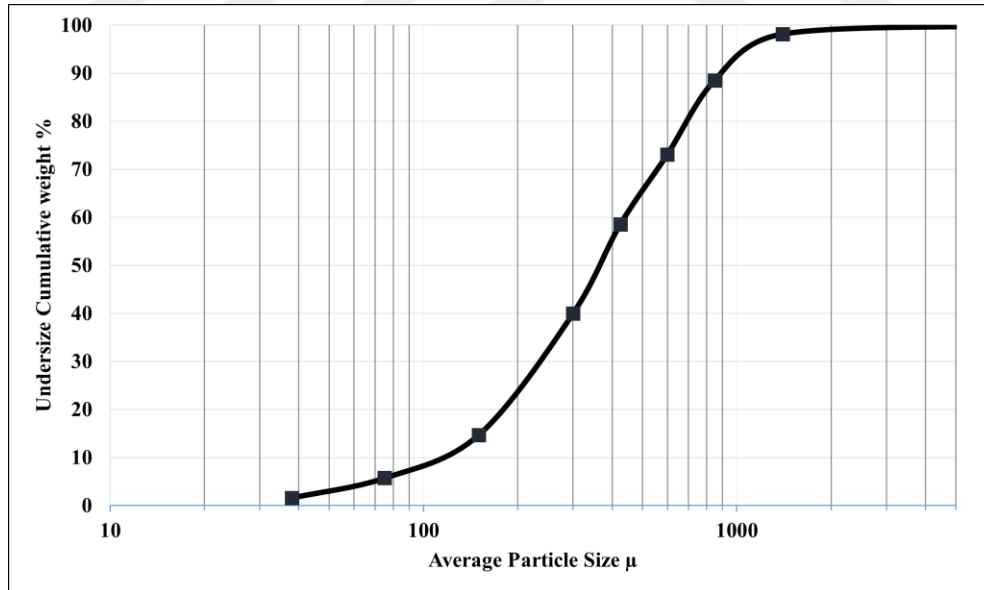


Figure 12. Particle size distribution of the sample

The material corresponding to each size fraction was collected, dried, and weighed. The particle size distribution of the sample is illustrated in Figure 12. The graph clearly indicates that the sample is relatively coarse, with a median particle size of approximately 360 μ m. This observation strongly implies that the gold present in the tailings is not

effectively liberated due to inadequate grinding processes employed at certain artisanal and small-scale gold mining (ASGM) sites. This deficiency in grinding significantly contributes to the low recovery achieved through amalgamation, along with the inefficiency of mercury usage.

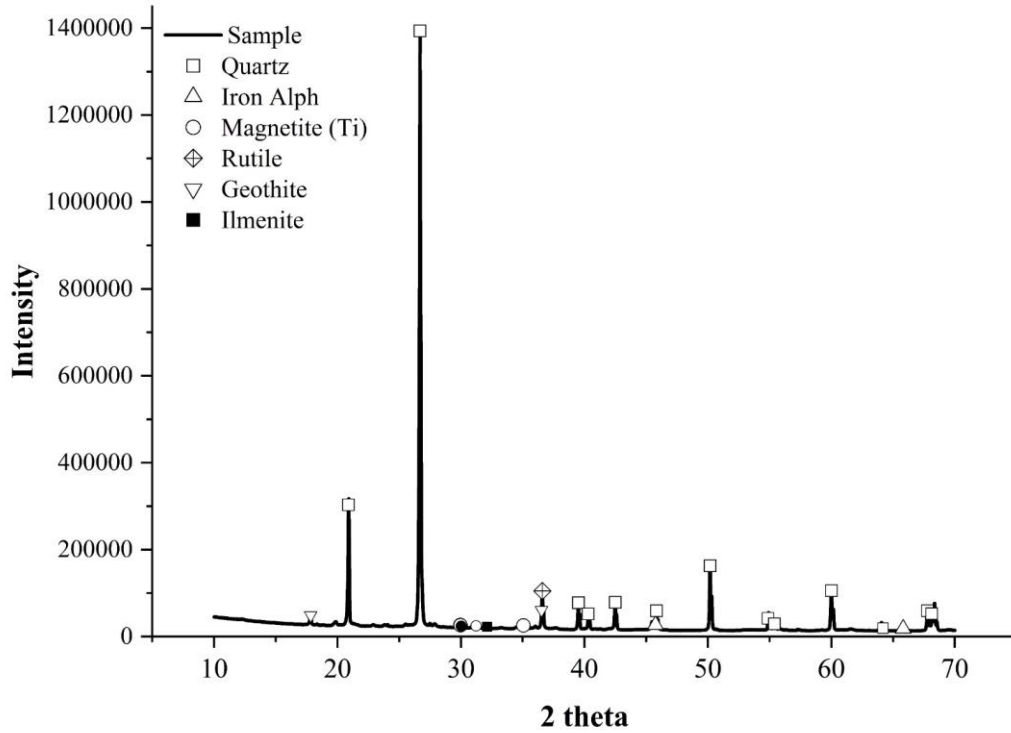


Figure 13. XRD profile of the ASGM tailings sample

Au grade was determined through fire assay analysis, while the other metals and elements were determined using acidic digestion-ICP analysis. The quantity of major oxides in the sample was ascertained by X-ray fluorescence (XRF). All these tests were conducted at ARGE TEST laboratories in Türkiye as it is shown in Table 6. The main component of the sample was found to be SiO_2 , accompanied by 9.65% and 5.8% of Al_2O_3 and Fe_2O_3 , respectively. Additionally, the sample contained less than 0.5% of Cr_2O_3 and TiO_2 . The grades of gold, silver, copper, and mercury were 14.45, 4.07, 275, and 8.2 ppm, respectively.

Mineralogically, as it is depicted in Figure 13, the sample primarily consists of Quartz. Furthermore, the analysis revealed the presence of various iron minerals including Goethite, Ilmenite, Magnetite, and Alph-iron. Moreover, the figure presented in the analysis highlights the identification of Rutile.

Table 6. Chemical composition of the sample

Compound	Grade %	Element	Grade ppm	Element	Grade ppm	Element	Grade %
Al ₂ O ₃	9.65	Au	14.45	Mo	16.7	Al	0.61
CaO ₂	0.04	Ag	4.07	Ni	16.89	Ca	0.02
SrO ₂	<0.01	As	4.8	Pb	51.9	Fe	3.12
BaO ₂	<0.01	Ba	168.1	Sb	129.8	K	0.29
Na ₂ O	<0.01	Be	<2	Sc	3.4	Mg	0.03
SO ₃	0.17	Bi	243.1	Sn	<5	Na	0.01
SiO ₂	78.07	Cd	<1	Sr	4.1	P	0.02
Fe ₂ O ₃	5.79	Co	45.9	Th	<5	S	0.07
MnO ₂	<0.01	Cu	274.9	Tl	<5		
Cr ₂ O ₃	0.03	Ga	<5	V	56.6		
MgO	0.54	Hg	8.2	W	<5		
P ₂ O ₅	0.06	La	9.9	Zn	31		
TiO ₂	0.21	Mn	724.4	Zr	5.4		
K ₂ O	3.38						
LOI	1.94						

3.5. Methods

3.5.1. Adsorbents Pretreatment

Initially, the resins underwent a thorough washing process using an abundant amount of distilled water to eliminate any potential debris from the resin beads that may have been generated during the manufacturing or transportation. Subsequently, the resins were subjected to a 2-hour washing period with 6 bed volumes of a 2 M NaCl solution to ensure complete conversion of the ion exchange active sites into chloride (Cl⁻) form. Following this,

an excessive amount of water was used to wash the resins for over two hours, aiming to remove any excess sodium chloride solution adhering to the beads. Prior to the sodium chloride pre-treatment, the weak base resins were washed with 5 BV of a 1 M HCl solution to ensure the protonation of all functional groups present on these resins. In the case of activated carbon, an extensive washing procedure with water was carried out to eliminate any fine particles from the bed. This was followed by a 2-hour washing period with 6 BV of a 2 M HCl solution, and finally, the activated carbon was washed with distilled water to remove any remaining traces of acid. Subsequently, all the adsorbents were dried in a temperature-controlled environment.

3.5.2. Original Solution Preparation

Applying the glycine leaching process the original PLS was produced from the sample. This involved the utilization of glycine as a lixiviant at a concentration of 2 g/l per 4 hours, along with potassium permanganate as an oxidant at the same concentration and duration. To modify the pH, sodium hydroxide and hydrochloric acid were used.

Table 7. ICP analysis of glycine PLS

Element	Conc. ppm	Element	Conc. ppm	Element	Conc. ppm
Au	1.925	Ca	1.80	K	>725.8
Ag	0.42	Fe	0.02	Mo	0.06
Hg	1.987	Ni	0.25	Ba	0.00
Na	>999.542	Zn	0.08	Sb	0.20
Be	0.01	U	0.03	Al	0.02
Mg	0.01	Pb	0.18	As	0.00
V	0.01	Se	0.26	Cd	0.00
Mn	0.29	Ti	0.55	Co	0.55
Cr	0.91	Cu	2.89		

The leaching procedure lasted for a total of 10 hours and was carried out under ambient temperature conditions. The pH of the solution was maintained at 10.5, while the stirring speed was set at 600 rpm. A solid/liquid ratio of 25% was maintained throughout the process. Following leaching, the resulting pulp underwent centrifugation before being transferred to an opaque glass bottle. It was then stored in a refrigerator until further use. The pregnant leach solution (PLS) obtained from this process was analysed using AAS, FIAS and ICP. The comprehensive results of these analyses are presented in Table 7. To ensure validity of the solution, a comparative analysis was conducted alongside all the experiments to verify that the composition of the PLS was not changed over time.

3.5.3. Synthetic Solution Preparation

Synthetic solutions were prepared for the purpose of conducting adsorption experiments, with specific initial concentrations of Au, Ag, Cu and Hg. Additionally, another solution was prepared for elution experiments, Table 8 shows the composition of the solutions. To prepare these solutions, precise amounts of 1000 ppm Au, Ag, Cu, and Hg standards were carefully measured using a high accuracy micropipette. These standards were then added to a beaker containing a solution of distilled water, along with 2 g/l of each glycine and potassium permanganate, at a pH of 10.5. The pH of the solution was adjusted using NaOH and HCl solutions. Subsequently, the beaker was placed on a magnetic stirrer, set at

Table 8. Composition of the synthetic solution

Solution	Au ppm	Ag ppm	Cu ppm	Hg ppm
Adsorption	3	1	3	2
Elution	7	2	1	7

400 rpm, for a duration of 6 hours to ensure the complete formation of Au, Ag, Cu, and Hg glycine complexes. To separate the MnO₂ precipitate from the solution, the solution was filtered using 0.45µm filter paper. The filtered solution was then transferred to an opaque glass container and stored in a refrigerator until needed. In order to determine the content of the solution, samples were taken and analysed. It was observed that, except for Cu, all other

metals effectively formed complexes, while a significant portion of Cu precipitated out of the solution.

3.5.4. Resins Screening Test

Seven different resins, as listed in Table (9) underwent a screening test to identify the most appropriate resins for the recovery of gold and mercury from glycine PLS. The test was conducted using a low resin-to-solution ratio of 1 g/l in order to create competition among the active sites of the resins. Specific quantities of the resins were introduced into a 100 ml conical flask, followed by the addition of a corresponding amount of synthetic solution with a pH of 10.5 to achieve the desired resin/solution ratio, as depicted in

Figure 14. The Conical flasks were then placed on an orbital shaker (Wiggen Hauser) operating at 200 rpm and a temperature of 25°C. After a contact time of 24 hours, samples were collected and analysed.

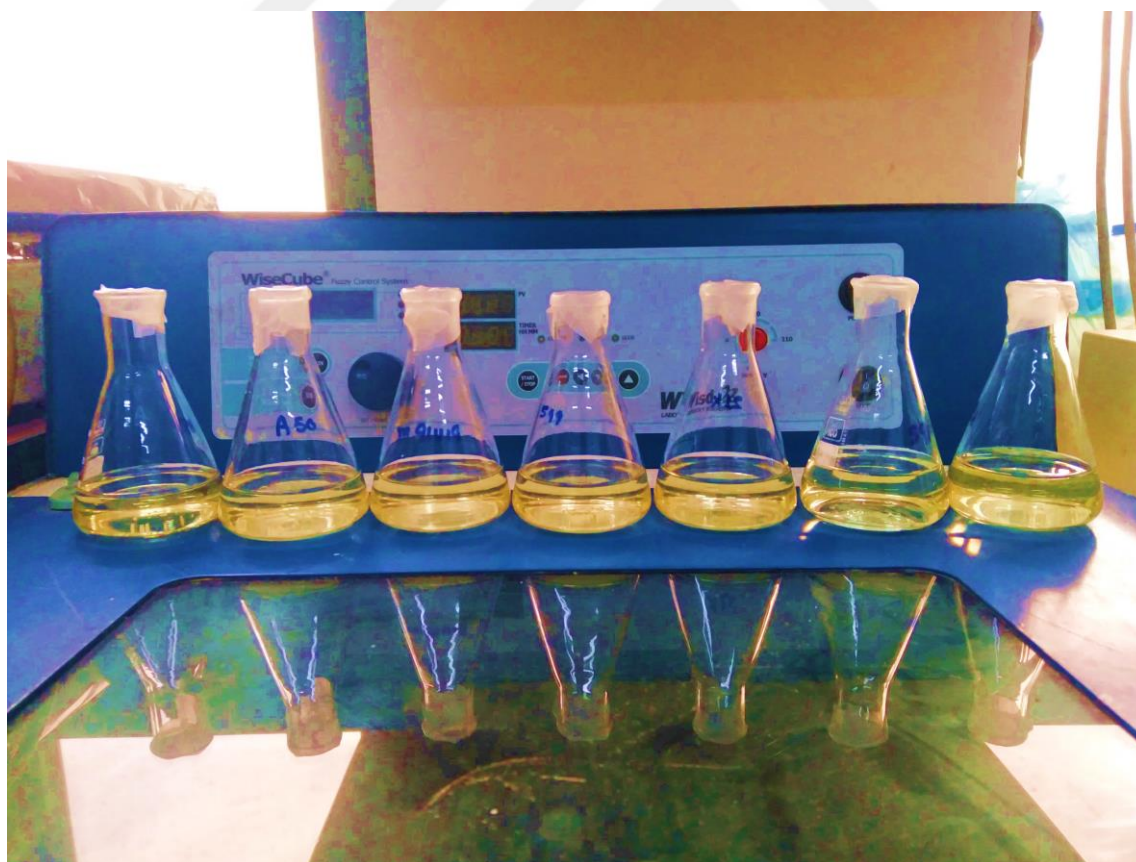


Figure 14. IX resins upon introducing to the screening test.

Table 9. Properties of the resins used in the screening test.

Resin	Phy. and Chem. Properties	FG	Cap. eq/L	MR %	pH
AmberSep 21K XLT	Macroporous, SB, Cl ⁻ form	QA	-	49 - 59	0-14
AmberSep M91419	Macroporous, SB, Cl ⁻ form	QA	0.3	50 - 60	0-14
Puregold MTA1940	Macroporous, MB Cl ⁻ form	TA & QAm.	3	44 - 52	0-14
Purogold MTA1930	Macroporous, MB, Cl ⁻ form	TA & QAm	3.8	46 - 56	0-14
Purolite A500CPlus	Macroporous, SB Cl ⁻ form	QAm	1.1	54 - 65	0-14
Purolite S992	Macroporous, WB, chelating resin, FB form	MA	4.4	47 - 55	0 - 7
Puromet MTS9100	Macroporous, Chelating Resin, FB form	Amidoxime	40 g/L	52 - 60	-

Table 10. Results of the screening test

Resin	Metal adsorbed %			
	Au	Ag	Cu	Hg
AmberSep 21K XLT	100.0	88.4	23.6	17.84
AmberSep M91419	100.0	100.0	22.6	28.27
Purolite A500CPlus	100.0	100.0	32.0	18.15
Purolite MTA1930	96.9	91.4	19.3	27.62
Purolite MTA1940	93.5	84.7	18.2	26.85
Purolite MTS9100	9.8	0.4	11.1	13.81
Purolite S992	68.1	32.5	24.3	48.45

To determine the remaining concentration of metals in the solution. The percentage of metal recoveries was then calculated and utilized to determine the most suitable resin for the recovery of gold and mercury, taking into consideration the downstream processes. Based on the findings presented in Table 10. Purolite A500CPlus and AmberSep M91419 resins were chosen for further experimentation and process development stages.

3.5.5. Adsorption Process Optimization

Once the appropriate adsorbent had been selected and the factors influencing the adsorption process had been identified, a series of experiments were conducted to optimize the process parameters. This was achieved by utilizing the full central composite design (CCD) on Minitab 20 Statistical Software, with a two-sided confidence level of 95 ($\alpha=0.05$). The parameters under investigation included temperature, pH, resin amount, adsorption time, and shaking speed.

$$R = \frac{C_o - C_t}{C_o} * 100 \quad (27)$$

Table 11. Coded and the uncoded values of the parameters.

Parameter	Coded form				
	2	1	0	-1	-2
Uncoded form					
Temperature ± 1 °C	49	40	30	20	11
pH ± 0.5	13.35	12	10.5	9	7.65
Absorbent g/l	3.9	3	2	1	0.1
Time hour	23.4	18	12	6	0.6
Shaking rpm	245	200	150	100	55

Based on the number of parameters being studied, the software recommended the execution of 52 experiments, which were classified as 32 Cube points, 10 Centre points in the cube, and 10 axial points, each parameter was examined at five different points, as

summarized in Table 11. Throughout these experiments, a synthetic solution containing 3 ppm Au, 1 ppm Ag, 3 ppm Cu, and 2 ppm Hg was utilized. The pH was adjusted at the beginning and during the experiment using NaOH and HCl. The temperature and shaking speed were monitored using a Wiggen Hauser orbital shaker. Additionally, the ratio of resin to solution was adjusted by weighing the resin and subsequently adding the synthetic solution as required. At the end of each experiment, a sample was taken and analysed. The metal recoveries were then calculated and inputted into the software for statistical analysis. The objective of this analysis was to optimize the process by selecting the best conditions that would yield minimum Cu recovery and maximum Au, Ag, and Hg recovery based on Equation (27). These optimal conditions would subsequently be employed in the next experiment, both with the original and synthetic solution.

3.5.6. Adsorption Kinetics Test

The purpose of this study was to generate a kinetic profile for the adsorption of both Au and Hg using three different adsorbents: Purolite A500CPlus, AmberSep M91419, and AC. Synthetic solutions with varying concentrations of Au and Hg were prepared for the experiment. Four solutions were created with Au concentrations of 1, 3, 5, and 7 ppm, while maintaining consistent Ag and Cu Hg concentrations of approximately 1, 5, and 2 ppm, respectively. Additionally, three solutions were prepared with different mercury concentrations of 1, 4, and 8 ppm, while keeping the Au, Ag, and Cu concentrations consistent at 3, 1, and 5 ppm, respectively. Before conducting each experiment, the pH of the synthetic solutions was adjusted to 10.5 using NaOH and HCl. A specific amount of the adsorbents was then introduced into separate conical flasks, and solutions were added to maintain a solution-to-resin ratio of approximately 500. The conical flasks were placed in a temperature-controlled orbital shaker (Wiggen Hauser) set at a temperature of 30°C and a shaking speed of 150 rpm. The experiment was conducted over a period of 24 hours. At specific time intervals (1, 2, 3, 6, 12, and 24 hours), samples were taken and analysed. The uptake of Au, Hg, Ag, and Cu onto the adsorbents was calculated to generate adsorption profiles. Furthermore, the adsorption data was fitted to Pseudo First-Order (PFO) and second order (PSO) adsorption models to gain a better understanding of the adsorption process.

3.5.7. Adsorption Isotherms

In order to gain a better understanding of the adsorption mechanism, valuable information can be obtained through the use of adsorption isotherms models. In this particular study, the Langmuir and Freundlich adsorption isotherm models were employed. To generate the necessary data for model fitting, a total of seven solutions were prepared, each with varying concentrations of Au (1, 3, 5, 7, 10, 18, and 38 ppm). The concentrations of Ag, Cu, and Hg were held constant at 1, 5, and 2 ppm respectively. Each solution was brought into contact with a specific amount of the three adsorbents (0.1 g). The experimental conditions included a temperature of 30°C, a pH of 10.5 adsorbent dosage of 2g/l, and a shaking speed of 150 rpm. After a period of 24 hours, equilibrium was reached. Subsequently, samples were taken and analysed. The equilibrium concentration C_e and the adsorbed amount of gold, q_e were then calculated. The obtained data were fitted to both the Langmuir adsorption isotherm model (LAIM) and the Freundlich adsorption isotherm model (FAIM). Finally, the parameters of each model were calculated.

3.5.8. Mercury Elution Preliminary Tests

Following the successful optimization of adsorption experiments and loading of gold and mercury onto ion exchange resins and active carbon, it is necessary to develop a selective desorption process for the sequential elution of gold and mercury. Extensive literature reviews have indicated that mercury can be effectively eluted using various types of acids. In light of this information, a pretest was designed utilizing HCl, H₂SO₄, and HNO₃ as potential eluents.

Before conducting the preliminary elution test, implementing the optimal conditions of the adsorption process, the three adsorbents were loaded with metals using a synthetic solution containing 7 ppm of Au, 2 ppm of Ag, 5 ppm of Cu, and 7 ppm of Hg, respectively. This step prepared the adsorbents for the subsequent elution preliminary tests. Subsequently, eluent with a concentration of 2 M was prepared from each acid. A specific amount of the loaded ion exchange resins and active carbon was weighed and placed in a conical flask, followed by the addition of 40 bed volumes (BV) of the eluent. To prevent any potential atmospheric interaction or evaporation, the flasks were covered with parafilm and placed in a Wiggen Hauser orbital shaker at a temperature of 25 °C and a shaking speed of 200 rpm. After a duration of 4 hours, the experiment was halted, and samples were taken for analysis.

The recoveries were then calculated to assess the effectiveness of the acids in selectively eluting mercury. The elution of the metals was calculated based on the Equation (28).

$$E\% = \frac{Q_L}{Q_s} * 100 \quad (28)$$

Based on the results obtained from the preliminary tests, H₂SO₄ exhibited a high level of selectivity towards mercury, while HNO₃ also demonstrated effectiveness but with lower selectivity. Consequently, H₂SO₄ was chosen for further comprehensive studies. Also, the AC activated carbon was executed due to the difficulty of its elution, and the downstream test were conducted only on IX resins. Furthermore, the AC was excluded from the subsequent tests due to the challenges associated with its elution, and the subsequent experiments were exclusively conducted on IX resins.

3.5.9. Mercury Elution Experiment

Following the selection of the eluent, a series of elution experiments were devised to examine the impact of various factors, including eluent concentration, bed volume, elution time, and temperature, on the removal of mercury, gold, and silver from Purolite A500CPlus and AmberSep 91419 using H₂SO₄. The investigation encompassed a range of 0.25 – 2 M for eluent concentration, 20 - 50 BV for bed volume, 2 – 8 hours for elution time, and 25 - 55 °C for temperature. By altering one parameter at a time while maintaining the other parameters constant at a value of 2 M for eluent concentration, 40 BV for bed volume, 4 hours for elution time, and a temperature of 25 °C, a total of 16 experiments were generated. All experiments were conducted in a temperature-controller Wiggen Hauser orbital shaker. The samples were analysed. And the impact of these parameters on the removal of mercury and other metals was observed.

3.5.10. Gold Elution Preliminary Tests

After the successful elution of Mercury, additional primary experiments were conducted to assess the effectiveness of various nominated eluents in extracting gold from IX resins. These eluents included acidic thiourea, sodium hypochlorite, and sodium perchlorate. For the experiment, four different eluents were prepared. The first eluent

consisted of a mixture of 0.75% v/v NaOCl, 150g/l NaCl and 5g/l NaOH. The second eluent was 2M NaClO₄, while the third eluent was a combination of NaClO₄ and 10 g/l of NaOH. The fourth eluent utilized well-known acidic thiourea with 2M H₂SO₄ and 2M thiourea.

A predetermined weight of loaded IX resins and AC was taken after the elution of mercury. These samples were then transferred to tightly closed tubes, and each tube was supplemented with an equivalent of 40 BV of the respective eluent. The elution vessels were securely covered with multi-layer parafilm and placed in a Wiggen Hauser orbital shaker, operating at a shaking speed of 200rpm and a temperature of 40 °C. After a duration of 12 hours, the experiment was concluded, and samples were collected for analysis. Following the necessary calculations and comparisons, it was determined that the mixture of 0.75% v/v NaOCl, 150g/l NaCl, and 5g/l NaOH exhibited the most favourable results as an eluent for future elution experiments.

3.5.11. Gold Elution Experiments

The primary objective of the gold elution experiments was to investigate the impact of various factors on the elution of gold from IX resins and identify the optimal conditions for maximizing gold recovery. Five factors were considered in this study, namely the concentration of NaCl, the concentration of NaOCl, eluent BV, retention time, and temperature. To maintain consistency in the experimental conditions, a plan was devised where one parameter was altered while keeping all other conditions constant. The eluent combination consisted of 0.75% v/v NaOCl, 150g/l NaCl, and 5g/l NaOH. The eluent volume, retention time, and temperature were maintained at 40BV, 12 hours, and 40 °C, respectively. Each factor was examined at four different points within specific ranges: NaCl concentration (50 – 200 g/l), NaOCl concentration (0.25 – 1% v/v), eluent volume (20 – 80 BV), elution time (6 – 24 hours), and elution temperature (30 – 55 °C). In total, 20 experiments were designed to explore the effects of these factors.

The required bed volume was achieved by transferring a precise quantity of the loaded IX resin into a tightly sealed tube. followed by the addition of the corresponding amount of eluent. The tube was placed into a temperature-controller Wiggen Hauser orbital shaker as depicted in Figure 15. The obtained samples were analysed and the impact of these parameters on the elution of gold and other metals was thoroughly discussed.

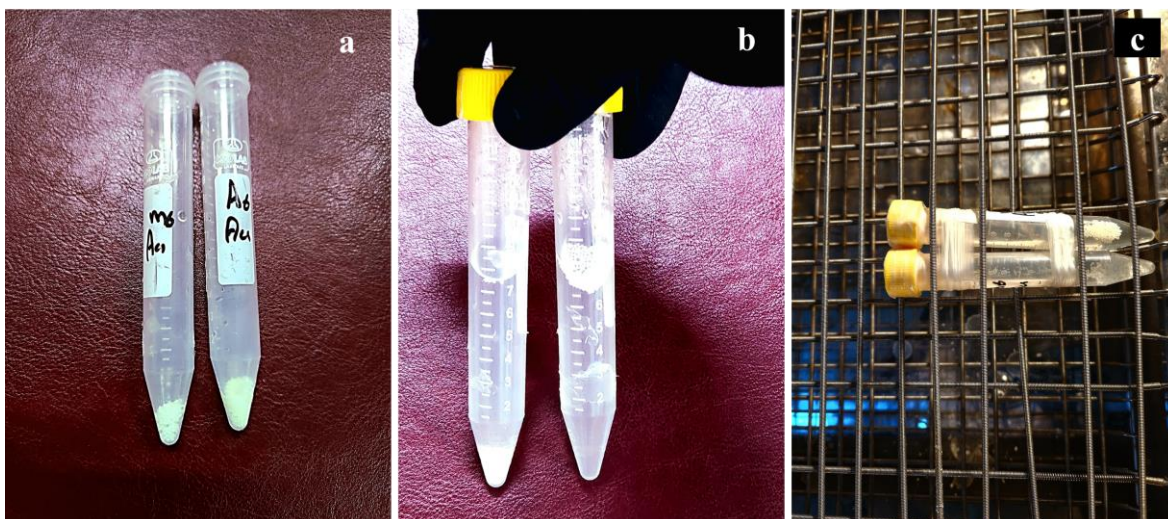


Figure 15. Gold elution experiments steps, placing resin to the tube (a), solution addition (b) placing the tube into orbital shaker (c).

3.5.12. Elution Kinetics

Elution kinetics were conducted to produce elution profiles for both Gold and Mercury. In the mercury elution kinetics test, IX resins were loaded with a synthetic solution containing 7 ppm of Au, 2 ppm of Ag, 5 ppm of Cu, and 7 ppm of Hg. A specific quantity of loaded Ion exchange resin was transferred to a tightly sealed plastic tube, followed by the addition of an equivalent amount of 40 BV of 0.25 M H_2SO_4 . The tubes were then placed in a temperature-controlled orbital shaker at a temperature of 25 °C and shaking speed of 200 rpm. Samples were collected at intervals of 0.25, 0.5, 1, 2, 3, and 4 hours. For Au elution, an equivalent of 80 BV of an elution solution containing 1% v/v NaOCl, 150g/l NaCl, and 5g/l NaOH was added. The tubes were then placed in a temperature-controlled orbital shaker at a temperature of 50 °C. Samples were taken at intervals of 1, 3, 6, 12, 18, and 24 hours. Subsequently, the samples were analysed, and the elution profiles were generated.

3.6. Cycle Test

The durability of the resins was evaluated through a series of cycle tests. During each cycle, the IX resins were loaded with a synthetic solution containing 7 ppm of Au, 2 ppm of Ag, 5 ppm of Cu, and 7 ppm of Hg. The loading process was carried out under optimal conditions that were determined beforehand. Subsequently, the resin was thoroughly washed

with distilled water and eluted with 0.25 M sulfuric acid to remove the Hg. The elution of mercury was conducted with an eluent volume of 40 BV, a retention time of 4 hours, a temperature of 25°C, and a shaking speed of 200 rpm. Following this step, the resin was again washed with ample distilled water and eluted with a solution consisting of 1% v/v NaOCl, 150g/l NaCl, and 5g/l NaOH. This elution process was performed with an eluent volume of 80 BV, a retention time of 24 hours, a temperature of 50°C, and a shaking speed of 200 rpm. The entire process was repeated five times. After any experiment, samples were collected and analysed. The elution% was then calculated for each cycle. Furthermore, the resins' capacity for metal adsorption after the elution process was assessed by determining the regeneration efficiency (RE%) using Equation (29).

$$RE = \frac{Q_r}{Q_o} * 100 \quad (29)$$

3.7. Analysis and Characterization

3.7.1. Analysis Method

The concentrations of mercury in the prepared solutions were determined using the Perkin Elmer AAS AAnalyst 400 Atomic Absorption Spectrometer and the Perkin Elmer/FIAS100 Flow Injection-Atomic Spectroscopy System technique. Prior to each analysis, calibration solutions were prepared at concentrations of 10 ppb, 20 ppb, 30 ppb, and 40 ppb using the High Purity Standards 1000 ppm Hg solution and a 2% HNO₃ solution. Calibration curves were then made by plotting the concentration and absorbance values of the standard solutions, as shown in Figure 16, a calibration curve regenerated from a data taken from (Kantarci, 2020). Based on these calibration curves, the concentrations of the samples were determined. During the analysis, argon gas with a purity of 99.996% was used as a carrier gas. The analysis of mercury was conducted under specific conditions, including a wavelength of 253.7 nm, a quartz cell temperature of 100 °C, a volume diluted carrier solution of 3% HCl (v/v), a reducing solution of 2% NaBH₄, and a 0.05% NaOH solution. The sensitivity of the analysis was approximately 0.07 absorbance for a 10 ppb Hg solution (Kantarci, 2020).

According to the requirements of ISO Guide 8466, the correlation coefficient R^2 of the curves of these calibration solutions should be greater than 0.995. After 20 measurements (analysed repeatedly) with 10 ppb calibration solution, the limits of detection (LOD) and limits of quantification (LOQ) to be 0.8 and 2.6 respectively (Alp et al, 2022). If the concentrations of the samples exceeded the highest calibration value, they were diluted to fit within the range of the calibration values. Two readings were taken for each measurement, and these readings were averaged.

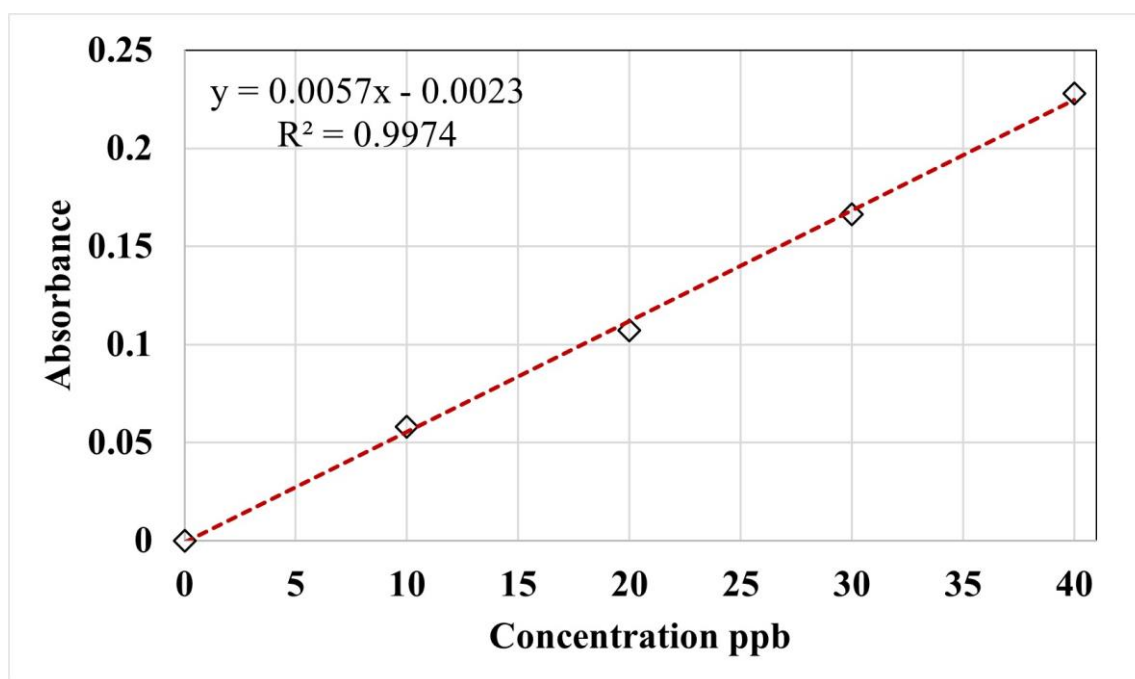


Figure 16. Hg Calibration curve of FIAS 100

The sample underwent Au, Ag, and Cu analyses using a Perkin Elmer AAS AAnalst 400 Atomic Absorption Spectrometer. To prepare the calibration solutions, Merck brand standard solutions with a concentration of 1000 (± 2) ppm Au, Ag, and Cu were utilized, resulting in calibration solutions of 0.5 ppm, 2.5 ppm, and 5 ppm for each element. Prior to sample readings, a calibration was performed for each element separately, achieving a correlation coefficient of $R^2 \geq 0.999$. Two readings were taken and averaged for each measurement. Acetylene (C_2H_2) at a flow rate of 2.54 L/min and air at a flow rate of 10 L/min, obtained from the compressor, were employed to atomize the elements in the solution. The wavelength and slit values used for Cu analyses were 324.75 nm and 2.7/0.8, respectively. For Au, the values were 242.80 nm and 2.7/1.35, while for Ag, they were

328.07 nm and 2.7/0.8. These values were selected based on the manufacturer's recommended conditions.

3.7.2. Adsorbents Characterization

In order to gain a deeper understanding of the adsorption mechanism and to diagnose the physical conditions of the fresh, loaded, and eluted adsorbents, a series of characterization tests were conducted. The first test was Fourier-transform infrared spectroscopy (FTIR). was performed to observe any changes in the bonding of the adsorbent throughout the various stages of the adsorption-desorption process using the IRSpirit-SHIMAZDU instrument operated by Karadeniz Technical University Central Laboratory. This analysis also aimed to determine the locations where metals were adsorbed. Additionally, scanning electron microscope (SEM) (JEOL brand JSM 6610 model) and energy-dispersive X-ray spectroscopy (EDS) (Oxford Instruments Inca X-act system) techniques were utilized to visualize the adsorbent and assess its physical condition, particularly after undergoing cycle tests. These methods were also effective in confirming the absence of metals in the eluted adsorbents, thereby validating the success of the elution process.

4. RESULTS AND DISCUSSIONS

4.1. Resins Screening Test

Among the resins currently in use, the strong base resins AmberSep 21K XLT, AmberSep M91419, and Purolite A500CPlus have demonstrated the highest recovery rates for Au and Ag, as it is represented in Table 12. These resins are particularly favoured for their ability to retain water, which is beneficial for monovalent Au and Ag glycine complexes. These complexes, due to their low charge, exhibit greater hydrophobicity compared to divalent and trivalent complexes. On the other hand, Purolite MTA1940 and Purolite MTA1930 possess mixed amine functional groups and offer higher capacity than the aforementioned strong base resins.

Table 12. Results of the screening test, resin 1 g/l, pH 10.5, temperature 25 °C, shaking speed 200 rpm.

Resin	Metal adsorbed %			
	Au	Ag	Cu	Hg
AmberSep 21K XLT	100.0	88.4	23.6	17.84
AmberSep M91419	100.0	100	22.6	28.27
Purolite A500CPlus	100.0	100	32.0	18.15
Purolite MTA1930	96.9	91.4	19.3	27.62
Purolite MTA1940	93.5	84.7	18.2	26.85
Purolite MTS9100	9.8	0.4	11.1	13.81
Purolite S992	68.1	32.5	24.3	48.45

However, this higher capacity also makes them less selective, allowing other monovalent complexes in the pregnant leach solution (PLS) to compete with Au and Ag for active sites. The remaining two resins are in free-base form, making them susceptible to vulnerability in high pH environments. In particular, Purolite S992 is designed to function optimally at a pH of 7. Based on these findings, AmberSep M91419 and Purolite A500CPlus

have been selected for further experimentation. It is worth noting that if the solution-to-resin ratio is maximized to reach 2 g/l, complete adsorption of Au, Ag, and Hg from the solution can be achieved. Starting from this juncture, the forthcoming adsorption experiments will incorporate both resins alongside activated carbon.

4.2. Adsorption Experiments Results

The present study focused on examining the impact of five different factors, namely temperature °C, pH, adsorbent dose g/l, contact time hour, and shaking speed rpm, on the adsorption of gold and mercury from a synthetic solution. To analyse the results, the DOE approach was employed, specifically utilizing a full CCD at a two-sided confidence level of 95 ($\alpha=0.05$) on Minitab 20 Statistical Software. The summary of the models for the various adsorbents is presented in Table 13.

Table 13. Summary of Au and Hg adsorption models

Au				
Variable Absorbent	S	R²	R² (adj.)	R² (pred)
Purolite A500Cplus	6.6	71.77%	53.55%	0.00%
AmberSep M91419	8.6	65.40%	43.08%	0.00%
MF AC	7.8	89.22%	82.27%	57.52%
Hg				
Purolite A500Cplus	16.9	69.21%	49.34%	0.00%
AmberSep M91419	15.4	68.51%	48.19%	0.00%
MF AC	7.1	88.72%	81.44%	56.59%

Although all the models were statistically significant, the R² values were relatively low. This could be attributed to the insignificance of some linear interaction parameters, the lack of fit of the Two-way interactions model, in addition to the insignificance of the square

effect of some parameters, as indicated in Table 14. In the case of the linear and square interaction models, at least half of the parameters were found to be insignificant for the adsorption of gold and mercury onto resins. However, the situation differs for the AC adsorption models, where the presence of unimportant factors is comparatively lower.

Table 14. Analysis of Variance for the adsorption parameters' liner effect, square effect and Two-way interaction on Au and Hg adsorption.

Parameters	P-Value					
	Au			Hg		
	A500Cplus	M91419	AC	A500Cplus	M91419	AC
Model	0.000	0.004	0.000	0.001	0.001	0
Linear effect	0	0	0	0	0	0
tem.	0.934	0.404	0.201	0.033	0.505	0
pH	0.779	0.620	0.074	0	0.00	0.004
Resin	0.000	0.001	0	0.017	0.001	0
Time	0.003	0.006	0	0.243	0.024	0
Shaking	0.014	0.012	0	0.982	0.782	0.002
Square effect	0.004	0.006	0	0.026	0.005	0
tem*tem	0.083	0.099	0.112	0.545	0.859	0.626
pH*pH	0.071	0.114	0.158	0.225	0.653	0.657
resin*resin	0	0.001	0	0.006	0.003	0
time*time	0.398	0.122	0	0.144	0.021	0
shaking*shaking	0.754	0.583	0.019	0.741	0.315	0.025
2-Way Interaction	0.374	0.703	0.083	0.320	0.835	0.620
All parameters	Lack of fit			Lack of fit		

4.2.1. Effect of Temperature

The gold mining industry is globally practiced in areas with a wide range of temperatures. In this study, the impact of temperature was examined within the range of 11 – 49 °C. However, the statistical analysis revealed that temperature had an insignificant effect, as indicated in Table 14. Generally, the influence of temperature on gold adsorption onto resins and AC exhibited a similar pattern. There was a slight decrease followed by a subsequent increase when the temperature was changed from 11 to 30 and from 30 to 49 °C, as depicted in Figure 17. This suggests that the adsorption process is primarily controlled by particle diffusion, and the slight increase in adsorption with rising temperature is likely attributed to an accelerated diffusion rate (Walton, 1949) but the intraparticle diffusion model fitting done in this research has proven the opposite. These findings are consistent with previous research indicating that higher temperatures can have a positive impact on the adsorption (Walton, 1949). Also it has been concluded that the adsorption rate of Au and Ag on AC is controlled by pore diffusion within the temperature range of 25 – 50 °C (McDougall & Copperthwaite, 1980).

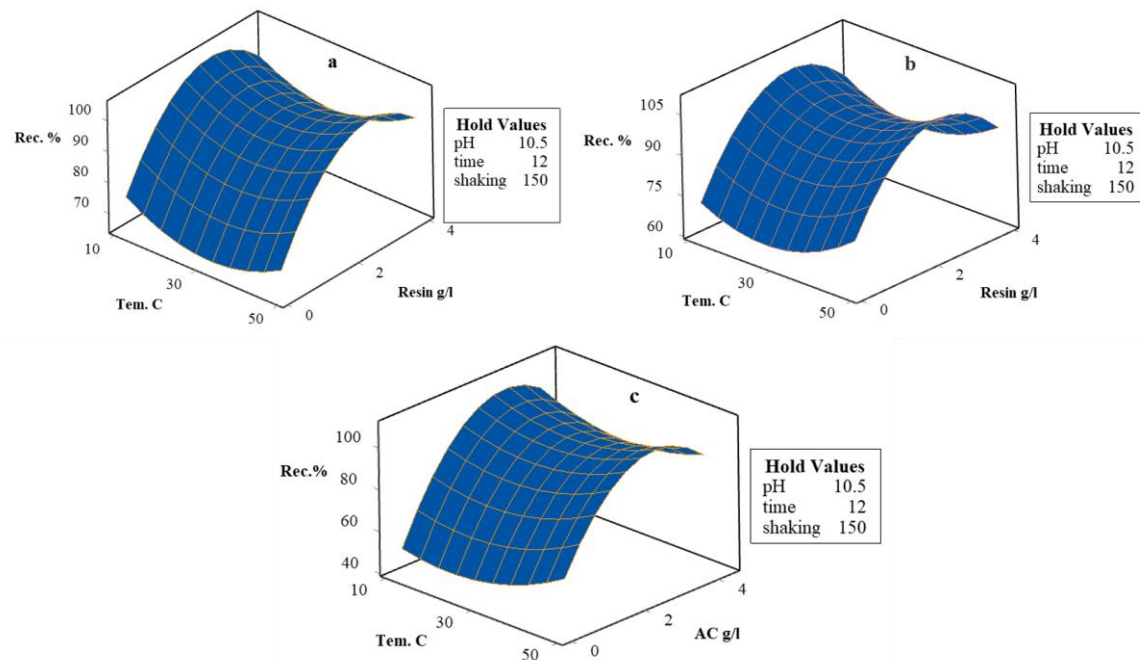


Figure 17. Surface Plot of Au adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of temperature (°C) and adsorbent dosage (g/l).

The graphs presented in Figure 18 clearly demonstrate a slight negative impact of temperature on the adsorption of the mercury-glycine complex on M91419 and AC. Moreover, the influence of temperature on the adsorption of mercury on A500Cplus resin is relatively higher. This observation can be attributed to two factors. Firstly, as the temperature increases, the resins tend to swell, thereby slowing down the diffusion process (Gaffney & Marley, 2014). However, it is important to note that no swelling phenomenon was observed during the experiment, as the resins used in this study only exhibit swelling in acidic conditions. Additionally, if swelling were to occur, it would have affected the adsorption of Au as well, which is not evident from the data presented in Figure 17. Another plausible explanation is that high temperatures destabilize the mercury-glycine complex due to its low stability constant, as reported by Gaffney and Marley (2014) with a log K value of 10.3 at 25 °C. This explanation appears to be more reasonable.

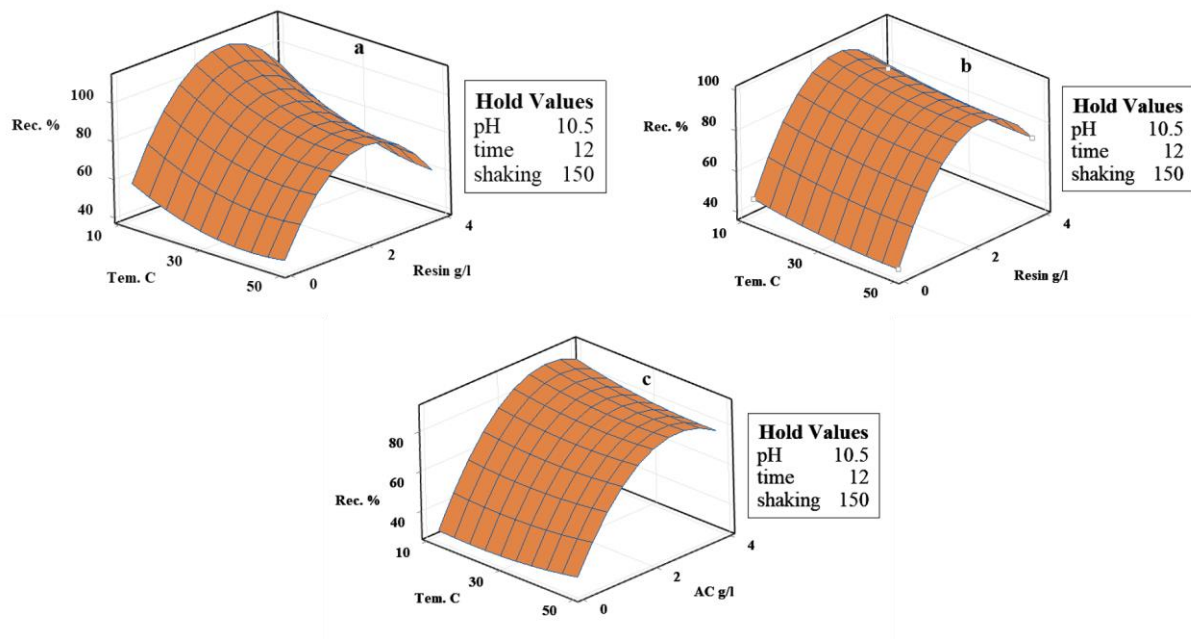


Figure 18. Surface Plot of Hg adsorption onto Purolite A500 CPlus (a), AmberSep M91419 (b) and AC (c). As function of temperature (°C) and adsorbent dosage (g/l).

While gold can be effectively adsorbed at both the low and high temperatures, it is noteworthy that mercury loading is more feasible at lower temperatures. However, these temperature ranges are not commonly found in most ASGM areas, making them impractical. Furthermore, the impact of temperature, as mentioned earlier, is not significantly influential.

Therefore, the temperature will be set at 30 °C. It is evident that at an adsorbent dosage of 2 g/l, a satisfactory uptake of both gold and mercury, close to 100%, can be achieved.

4.2.2. Effect of pH

Strong base ion exchange resins are renowned for their efficient performance across a wide pH range. Conversely, active carbon has been found to exhibit greater efficacy at lower pH levels (Marsden & House, 2006). The influence of pH within the range of 7.65 to 13.35 was thoroughly investigated, and it was determined that the pH had no statistically significant impact on the adsorption of Au by any of the adsorbents examined in this study. Figure 19 illustrates that gold recovery from the solution was high at lower pH values despite the slight decline experienced as the pH increases to 12. Subsequently, there is a faint increase in gold recovery as the pH further rises to 13.5.

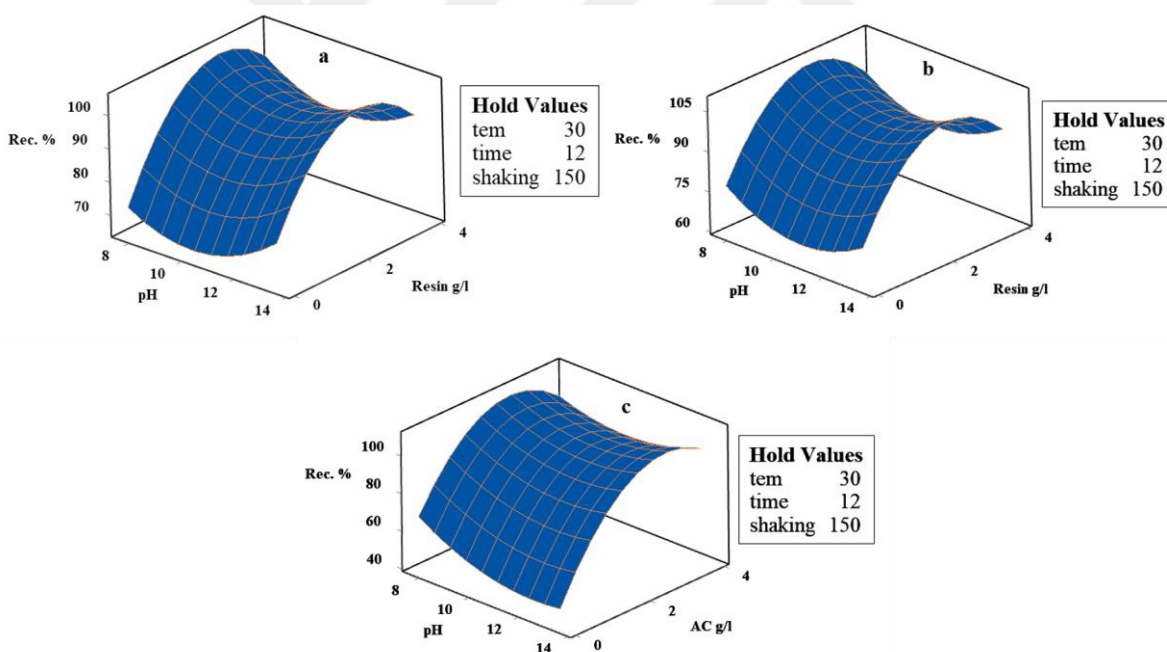


Figure 19. Surface Plot of Au adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of pH and adsorbent dosage (g/l).

The decrease in adsorption of Au with increasing pH can be attributed to the interface of OH⁻ ions with metal complexes, which compete for adsorption sites on the strong base ion exchange resins and AC. Another plausible explanation is the activation energy for Au adsorption on these resins, which is approximately 16.5 kJ/mol (Marsden & House, 2006).

This indicates that the adsorption process is controlled by boundary diffusion and may be influenced by the increase in solution viscosity resulting from the addition of NaOH to adjust the pH. However, the reasons behind the observed increase in Au recovery by the ion exchange resin as the pH exceeds 12 remain unclear.

As anticipated, the impact of pH on the adsorption of Au on AC is negative. However, it is not statistically momentous. Numerous publications, including the one authored by McDougall and Copperthwaite in 1980, have proposed that electrostatic interactions play a role in the adsorption of gold cyanide complexes on AC in both acidic and basic environments. Consequently, an increase in pH results in a reduction of positive sites on the AC granules, leading to a decrease in the attraction of Au-cyanide (McDougall & Copperthwaite, 1980). This explanation can also be applied to account for the decrease in adsorption rate on AC with increasing pH, considering the similarities between the adsorption mechanisms of Au-glycine and Au-cyanide. These findings align closely with the observations made by Tauetsile (2018) during their investigation of gold adsorption behaviour on AC from a solution containing 2 ppm Au, 40 ppm Cu, and 5 g/L glycine, at a temperature of 23 °C, over a duration of 24 hours, they concluded that increasing the pH gradually from 9 to 12 had a negative effect, they attributed the decrease for the same reasons stated above. The activation energy for gold adsorption on AC is generally around 11 kJ/mol, falling within the range of mass transfer-controlled adsorption, as described by Marsden and House in 2006. This explains the higher kinetics observed for ion exchange (IX) compared to AC, attributed to the larger size of the AC granules.

The significance of pH in mercury adsorption cannot be overstated. According to the findings presented in Table 14, It greatly enhanced the adsorption of Hg on resins, while having a moderate effect on active charcoal, as depicted in Figure 20. Interestingly, this effect is completely contrary to its influence on the adsorption of Au. Regrettably, there is a lack of available data regarding the behaviour of mercury-glycine adsorption on resins and AC. Therefore, further investigations will be necessary to explain this phenomenon. Consequently, the understanding of how pH affects the adsorption Hg onto IX and AC will rely on previous studies done on different PLS.

The first possible explanation can be derived from a study done by (Javidi Alsadi & Esfandiari, 2019), this study agrees with what has been found in this research. The increase of the mercury adsorption in accordance with the pH was attributed to two possible reasons. The abundance of the OH⁻ ions in the medium, which leads to the formation of the COOH

group, along with the existence of the Cl^- on the active site of the resin, and the oxygen led to increase the mercury adsorption on AC and resins respectively.

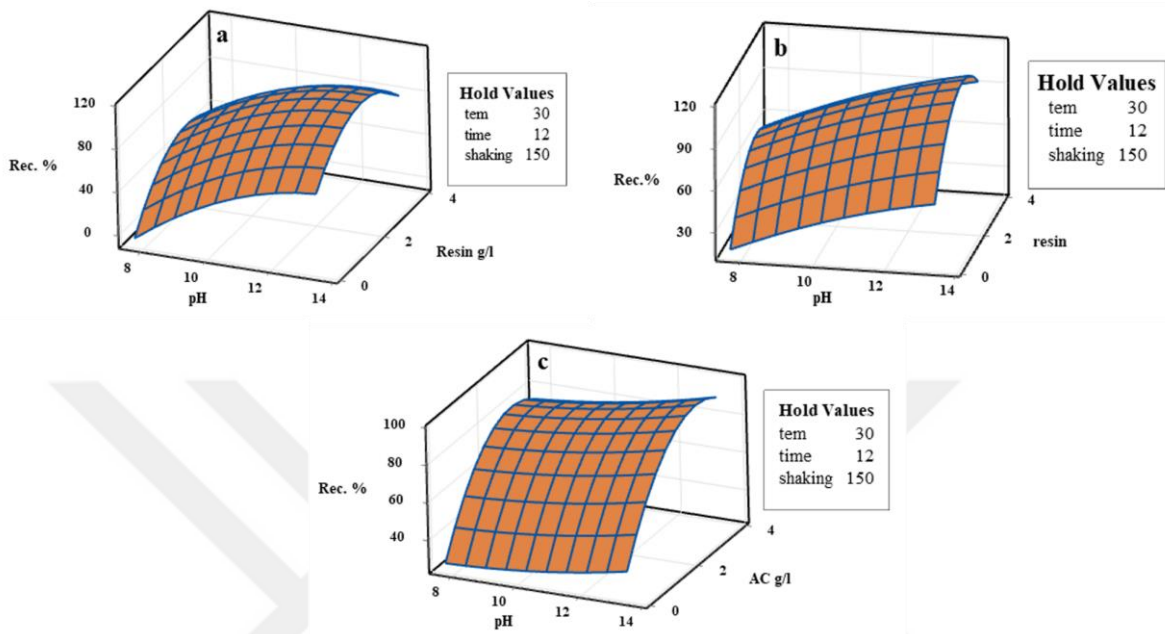
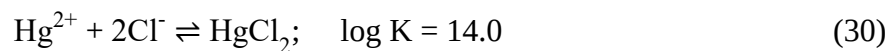


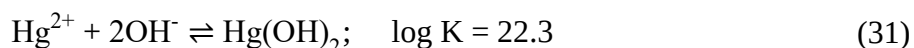
Figure 20. Surface Plot of Hg adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As a function of pH and adsorbent dosage (g/l).

In a study conducted by (López-Muñoz et al., 2011) to uptake Hg(II) from HgCl_2 solutions using the heterogeneous photocatalysis with TiO_2 , as a function of many factors including the pH in the range (2 - 10). They found that the structure of mercury species changes hugely with changing the pH. As the pH increases from (7 – 14), the solution's speciation changes gradually from HgCl_2 (log $K = 14$) to Hg(OH)_2 (log $K = 22.3$), as represented in Equations (30) and (31). Based on this explanation, it can be inferred that if mercury hydroxide can become the predominant species in a mercuric chloride solution with a log K value of 22.3 at high pH, it is highly likely to dominate in a less stable mercuric glycine solution with a log k value of 10. Due to its superior stability, Hg(OH)_2 exhibits a higher adsorption capacity on both IX and AC compared to the mercury-glycinate complex.



In general, the impact of pH on the absorption of Au was negligible. However, it plays a crucial role in the adsorption of Hg. Therefore, it is important to select the optimal pH that

guarantees acceptable Hg recovery, taking into account the pH of the leaching solution. Figure 19 demonstrates that pH has a substantial influence when the dosage of the adsorbent is extremely low. However, as the adsorbent dosage approaches 2 g/l, the effect of pH becomes less significant. By adjusting the pH to 10.5 and using an adsorbent dosage of 2 g/l, it is possible to achieve satisfactory Hg uptake without compromising the recovery of Au.



4.2.3. Effect of Adsorbent Dosage

The dosage of the adsorbent plays a critical role in the process of adsorption (Khosravi et al., 2017). According to the literature, increasing the adsorbent dosage will have a positive impact on the adsorption. This is because higher dosages provide more active sites for adsorption. In a study conducted by Tauetsile (2019), the effect of different concentrations of adsorbent (2, 4, 8, and 12 g/l) on the gold loading from a cyanide-starved glycine solution was investigated. The researchers found that the loading efficiency increased proportionally with the increase in adsorbent amount.

In this study, the effect of adsorbent dosage on the recovery of both Au and Hg was examined within the range of 0.1 to 3.9 g/l. Figure 21 clearly demonstrates that the recovery of gold by both IX and AC significantly improved as the adsorbent amount increased from 0.1 to 2 g/l. However, when the adsorbent dosage was further increased from 2 to 3.9 g/l, the gold recovery experienced a very slight decrease for unknown reasons.

Similarly, the adsorbent dosage also had a notable impact on the adsorption of mercury onto three different adsorbents, as shown in Figure 22. Initially, increasing the adsorbent dosage positively influenced the adsorption of mercury up to 2 g/l. However, beyond this point, the adsorption of mercury dramatically declined, particularly for the resins.

The decline in mercury absorption as the adsorbent dosage increases can be elucidated by considering the previously discussed pH effect. It has been observed that the adsorption of mercury is directly proportional to the pH level. When the concentration of the adsorbent is heightened, it leads to a reduction in the population of OH^- ions in the solution due to adsorption.

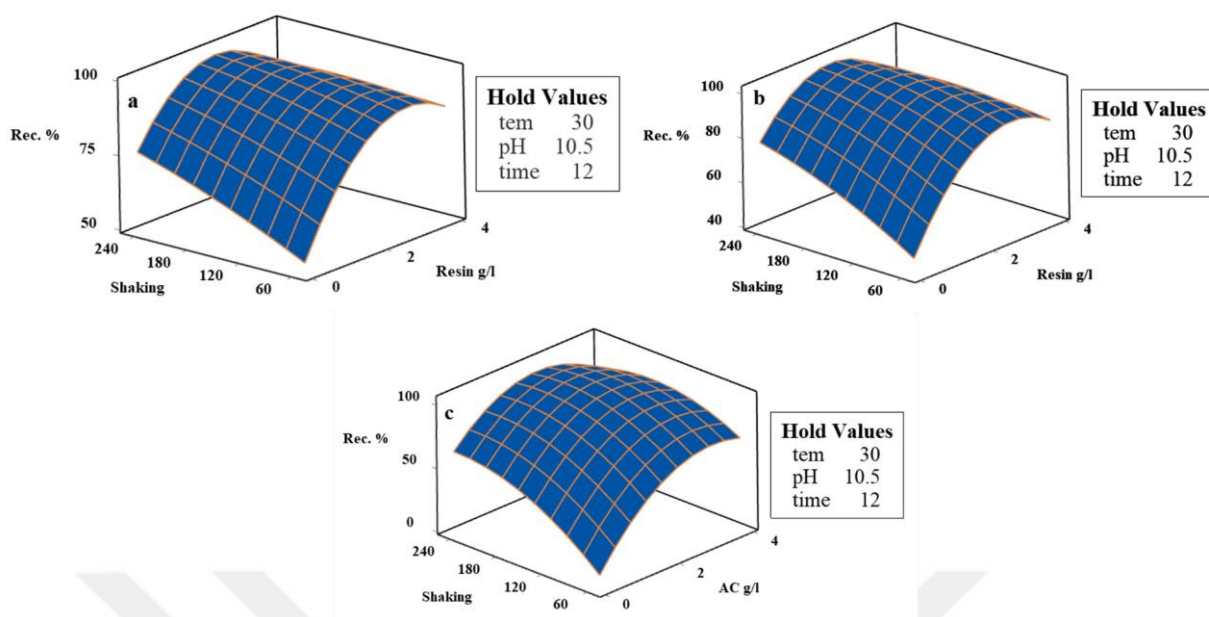


Figure 21. Surface Plot of Au adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of adsorbent dosage (g/l) and shaking speed (rpm).

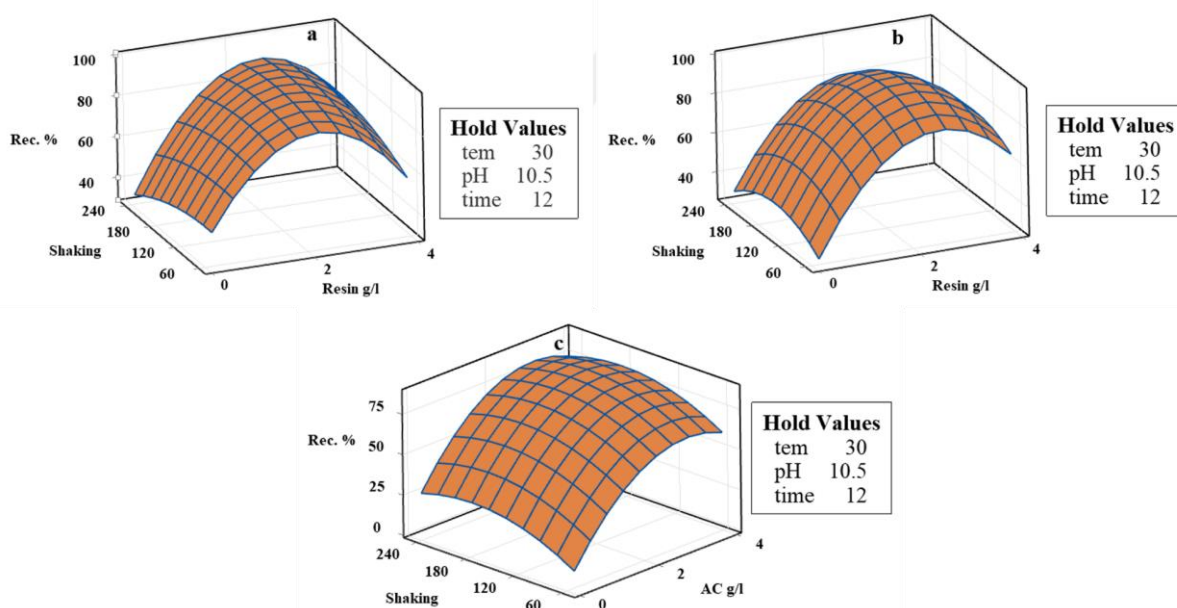


Figure 22. Surface Plot of Hg adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of adsorbent dosage (g/l) and shaking speed (rpm).

This can occur either by IX resins, which have the capability to exchange hydroxide ions in the solution with chloride ions from their functional groups, or AC, which is extensively documented in literature for its ability to electrostatically adsorb hydroxide ions. This decreases in OH^- ions will lower the pH level and consequently, decreases the loading

of mercury. It has been clearly demonstrate in Figure 21 and Figure 22 that the recovery rates of both Au and Hg increase steadily as the adsorbent dosage increases up to 2 g/l. Beyond this dosage, the recovery rates plateau or even decrease, indicating that 2 g/l is the optimal dosage for achieving maximum recovery.

4.2.4. Effect of Retention Time

The impact of time on the adsorption of gold and mercury complexes adsorption has been studied within the time frame of 0.5 to 24 hours. The statistical data in Table 14 and graph in Figure 23 clearly demonstrates that time plays a significant role in the Au adsorption process, particularly when it comes to activated carbon; While both resins are able to adsorb approximately 80% of the gold within the first hour when the adsorbent dosage is 2 g/l, activated carbon only manages to adsorb around 60%.

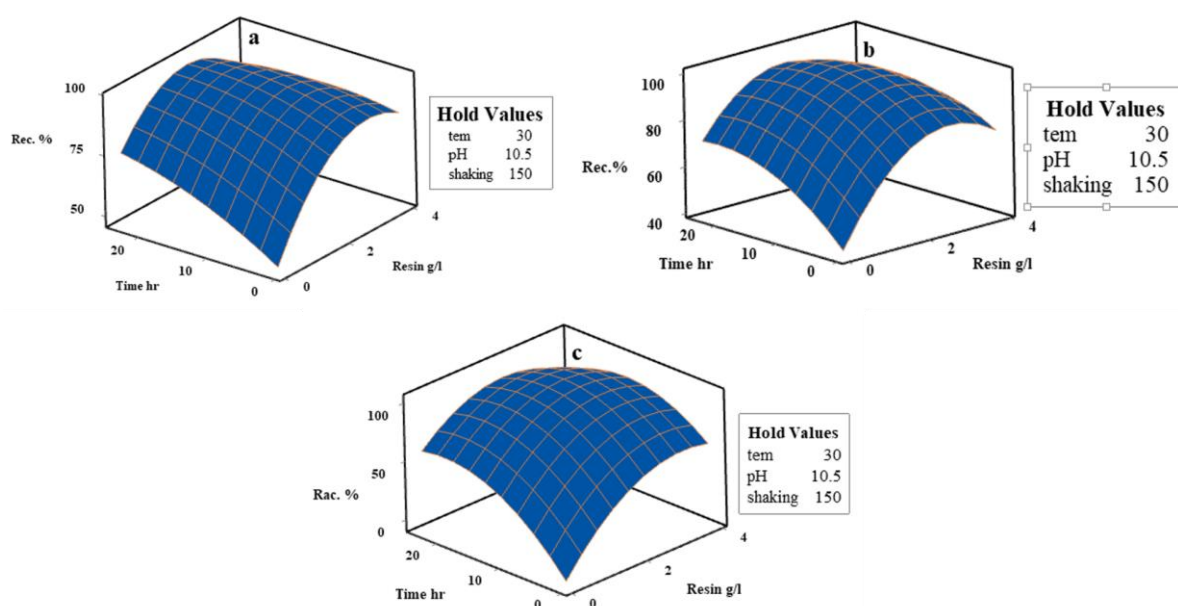


Figure 23. Surface Plot of Au adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of adsorbent dosage (g/l) and, contact time (hr).

This discrepancy can be attributed to the larger granule size of the carbon, which reduces the surface area available for adsorption compared to the resin beads. Furthermore, the carbon's larger granules possess deeper pores, resulting in a slower adsorption rate that necessitates more time for the adsorption process to reach equilibrium.

The loading rate of the mercury onto the three adsorbents was influenced by the retention time in a similar manner to that of Au. As observed in Figure 24, The of retention time impact on the loading of Hg onto the adsorbent can be ordered ascendingly as: Purolite A500, AmberSep 91419, and AC. This order is directly proportional to the particle size distribution of the adsorbent, which has been presented in materials section.

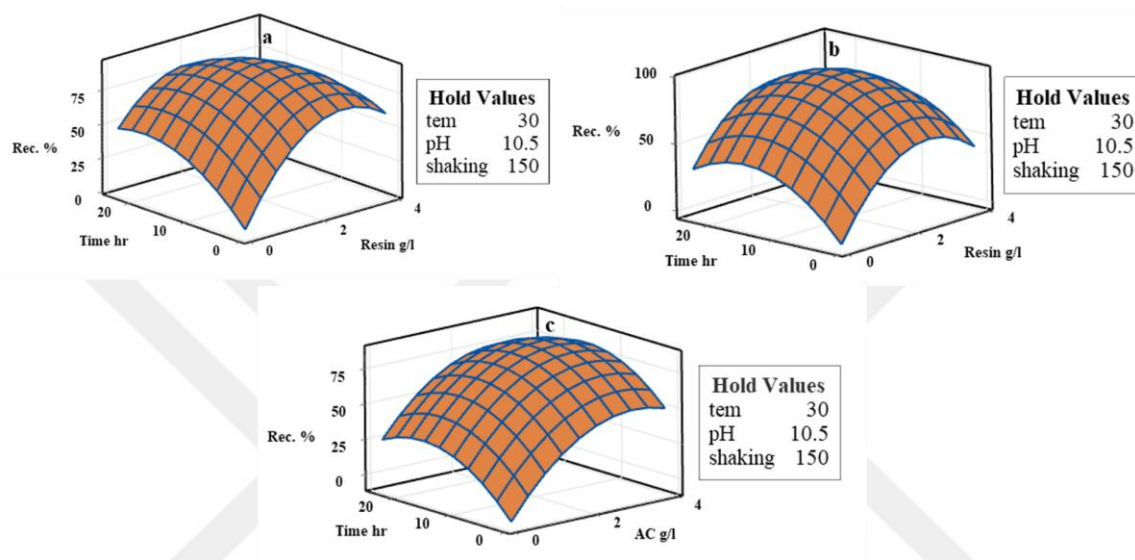


Figure 24. Surface Plot of Hg adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of adsorbent dosage (g/l) and contact time (hr).

It was commonly observed that the adsorption of both metals increased incrementally with the duration of time up to the 12th hour. However, beyond this period of time, there was no significant increase in adsorption, making it not worthwhile to extend the time further. It is important to note that the leaching process duration, as stated in recent publications, is 10 hours. Therefore, the optimum time for adsorption has been determined to be 12 hours. This approach allows for the completion of the entire process in a shorter time, resulting in reduced operational costs.

4.2.5. Effect of Shaking Speed

In their investigation on the recovery of Au-glycinate onto activated carbon, Tauetsile et al. (2018) maintained a bottle roll speed of 105 rpm. Conversely, Eksteen and Oraby (2015) conducted a separate study where the rolling speed of the bottle remained fixed at 150 rpm. In the present study, the impact of agitation speed on the loading of gold and

mercury on both AC and ion exchange resin (IX) was examined within the range of 50 – 250 rpm. The ANOVA values in Table 14 indicate the significance of the shaking speed for Au adsorption, and this is further supported by the data presented in Figure 25, which demonstrates the incrementally proportional effect of shaking speed on Au loading onto the three adsorbents. The adsorption of Au onto Purolite A500CPlus increased from 60% to 98%, and from 60% to 92% onto AmberSep M91419, while its loading onto AC increased from 10% to 70%, as the shaking speed increased from 50 to 250 rpm. This can be attributed to the reduction in film resistance to mass transfer at the liquid-solid interface due to the increase in shaking speed (Kyzas et al., 2020). Additionally, at lower shaking speeds, the sorbents remain static and have limited interaction with the metal ions, particularly in the upper part of the vessel.

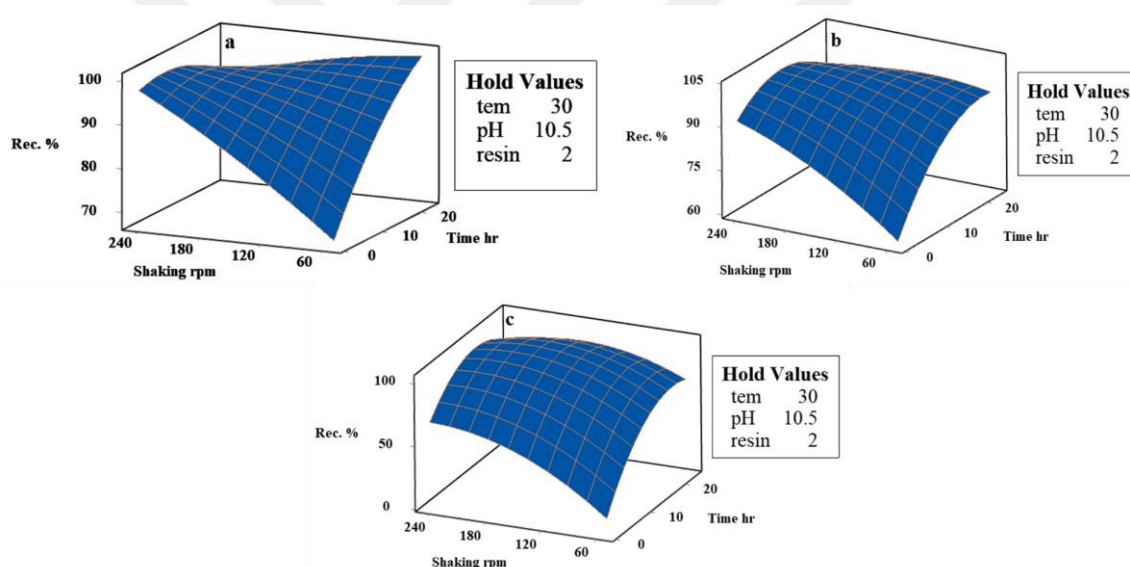


Figure 25. Surface Plot of Au adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of shaking speed (rpm) and, Contact time (hr).

The significance of this study becomes evident when compared to previous research conducted at different agitation speed ranges. Soleimani and Kaghazchi (2008) examined the effect of agitation speed on gold adsorption onto activated carbon within the range of 150 – 600 rpm and found that it did not significantly impact Au adsorption. Similarly, Khosravi et al. (2017) investigated the influence of agitation speed on gold adsorption onto activated carbon within the range of 35 – 55 rpm and obtained similar results. Therefore, this

study provides valuable insights into the effect of shaking speed within unexplored ranges, which were not previously investigated by either of the aforementioned research groups.

Based on the analysis of variance values, it can be concluded that the shaking speed between 50 to 250 rpm does not significantly impact the adsorption of mercury onto both IX and AC. Even when the shaking speed is increased from the minimum to the maximum at any point during the adsorption process, the increase in adsorption is only around 10% in the best cases as it is shown in Figure 26. This finding aligns with the conclusions drawn by Alsadi and Esfandiari (2019) in their study on the effect of agitation speed on mercury removal using activated carbon from aqueous solutions. Which emphasized the insignificance of agitation speed in mercury adsorption by AC.

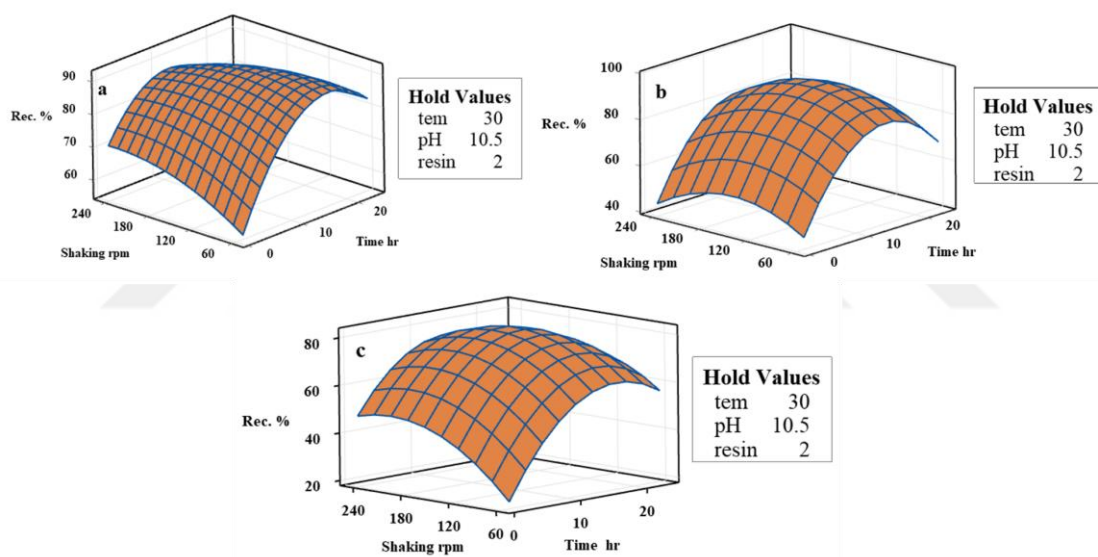


Figure 26. Surface Plot of Hg adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c). As function of shaking speed (rpm) and, Contact time (hr).

Considering that the optimum adsorption parameters have already been optimized before as adsorption environment temperature 30 °C, pH 10.5, adsorbent dosage 2 g/l, and 12 hours as adsorption time, the ideal shaking speed under these conditions is determined to be 150 rpm. Beyond this value, the recovery of gold does not improve, and below it, the recovery of mercury decreases. Under these conditions, the maximum Au and Hg adsorption were acquired, except for AC, which recorded a low recovery of Hg, around 80% and Cu around 50%. These results are consistent with the findings of Aliprandini. (2020), who conducted a study on recovering mercury from mercury cyanide synthetic solution using

granular AC. The synthetic solution used in these experiments contained metal complexes of Au, Ag, Cu, and Hg-glycine. The discussion primarily focused on Au and Hg complexes, as they were the main concern, while Ag and Cu exhibited similar adsorption behaviour to Au complexes. In other words, the optimal conditions that acquire the best gold and mercury uptake are also appropriate for achieving the best Ag adsorption.

4.2.6. Adsorption Kinetic Models

In order to investigate the adsorption kinetics of Au and Hg onto three different adsorbents, the study employed the PFO and PSO adsorption models. Initially, the impact of varying Au concentrations (1, 3, 5, and 7 ppm) was examined while maintaining Hg concentrations at 2 ppm. Subsequently, the effect of different Hg concentrations (1, 4, and 8 ppm) was studied while keeping the Au concentration constant at 3 ppm. The suitability of the model in relation to the adsorption data was assessed based on the correlation coefficient R^2 and the calculated adsorbed amount of the adsorbate at equilibrium (q_e , cal.) in milligrams per gram (mg/g). Additionally, the adsorption data was analysed using the intraparticle diffusion model (IPD) to determine the controlling step of the adsorption process. The results were presented in Tables 14, 15 and 16.

The findings revealed that the R^2 and q_e , Cal values of PFO for Au adsorption onto the three adsorbents were not satisfactory. Furthermore, the calculated adsorption equilibrium capacity was significantly lower than the experimental values. In contrast, the values obtained for PSO were adequately high, indicating that the adsorption of Au onto IX resins and activated carbon follows the PSO model. This observation aligns with the conclusions drawn by Deng, et al. (2020) in their study on the adsorption kinetics of Au from cyanide-starved glycine liquor at different Au concentrations using IXOS resin. They also found that the data fit the PSO model with an R^2 value of 0.999.

The results obtained from the experiments suggest that the adsorption process occurred through chemisorption and ion-exchange mechanisms (Khosravi et al., 2017; Deng et al., 2020). Furthermore, it was observed that the initial concentration of gold had a positive impact on the quantity of gold adsorbed Cal q_e , but it had a significantly negative effect on the rate constant k_2 . The positive influence on Cal q_e can be attributed to the increased driving force of gold concentration, leading to more gold being deposited onto the surface of the adsorbent. On the other hand, the negative effect on k_2 is a consequence of the system

requiring more time to reach equilibrium as the adsorbate concentration increases. This results in a decrease in the value of k_2 with higher concentrations (Khosravi et al., 2017). Based on the k_2 values, the order of adsorption kinetics can be ranked as follows: Purolite 500C+ resin > AmberSep91419 resin >> activated carbon. This discrepancy can be attributed to the grain size of the adsorbent, which plays a significant role in the adsorption kinetics.

At varying concentrations of gold, it was observed that the adsorption of mercury onto IX resins followed the PSO adsorption model and occurred through the same mechanism as gold. Conversely, the adsorption behaviour of mercury onto activated carbon fit both PFO and PSO models, with higher R^2 values for PFO at [Au] 7 ppm. This discrepancy may be attributed to the involvement of other mechanisms. The adsorption of metals-cyanide and metals-glycine onto activated carbon are known to occur through different mechanisms. This finding aligns with a study conducted by Salehi et al., (2020) on the adsorption of gold cyanide onto different types of activated carbon, where both PFO and PSO models showed high correlation coefficients R^2 and good agreement between the calculated and experimental equilibrium adsorption capacities (q_e , cal. q_e , exp.), yet no explanation was provided for this phenomenon. On the other hand, Aliprandini et al. (2020) also reported that the adsorption kinetics of $\text{Hg}(\text{CN})_2$ onto granular activated carbon fit the PSO model with an R^2 value of 0.999, compared to an R^2 value of 0.745 for PFO, and they suggested that the adsorption occurs through a chemisorption (ion-exchange) mechanism. It was noticed that the experimental equilibrium adsorption capacity values (q_e , exp.) of IX resins are higher than those of activated carbon, indicating a slower uptake of mercury by activated carbon compared to the resins.

The data provided in Tables 17, 18 and 19 display the PFO and PSO parameters obtained under various concentrations of Hg. It was observed that the changes in Hg concentration did not have any impact on the data fitting for both PSO and PFO, as well as the equilibrium adsorption capacity values q_e . The adsorption kinetics of both Au and Hg at different Hg concentrations still conformed to the PSO model, with R^2 values approaching unity for all the adsorbents. Furthermore, it was noticed that increasing Hg concentration did not affect the loading of Au onto neither of the adsorbents.

Moreover, the increase in Hg concentration affected both the calculated adsorption capacity q_e , cal and the K_2 values of Hg in a manner similar to altering the Au concentration

on Au q_e , cal. and the K_2 . The tables illustrate that the K_2 values for Hg adsorption decreased as the Hg concentration increased while those of Au remained approximately constant. Interestingly, when the Hg concentration was altered, the data for Hg adsorption onto AC only fit the PSO model, unlike the situation with altering Au concentration. This phenomenon requires further explanation.

The determination of the rate limiting step is crucial to understand the adsorption process. In this study, the intraparticle diffusion model was employed to analyse the data and identify the rate controlling step. Figure 27 illustrates the relationship between the adsorption capacity at any time q_t and the square root of time $t^{0.5}$ for the adsorption of Au onto IX resins and AC. Interestingly, the plot reveals multiple linear trends in the adsorption behaviour, suggesting that the adsorption occurs through different stages rather than being solely limited by intraparticle diffusion (IPD).

According to previous research conducted by Ramesh et al. (2008) and Khosravi (2017), the initial stage of the adsorption process involves the diffusion of Au ions from the solid-liquid interface to the surface of the adsorbent. The second linear stage is controlled by intraparticle diffusion, where the adsorption gradually takes place within the adsorbent particles. Finally, the slowest stage is attributed to the attainment of equilibrium, where the concentration of Au becomes extremely low, resulting in a declination of the IPD process (Ramesh et al. 2008, Khosravi et al. 2017). These findings align with the research conducted by Salehi et al. (2020) on the adsorption of gold-cyanide onto AC. The behaviour of Au adsorption onto both resins exhibits remarkable similarities, with R^2 values ranging from 0.57 to 44, depending on the concentration of Au. However, there is a slight variation in the case of activated carbon, which demonstrates higher R^2 values ranging from 0.69 to 0.81.

Figure 28 illustrates the IDP model for mercury adsorption onto IX and AC at varying Au concentrations. The multilinearity behaviour observed during Au adsorption is also evident in the adsorption of mercury onto IX resins. However, the adsorption manner of mercury onto AC showed a better fit to IPD compared to IX resins. The dissimilarity in the adsorption behaviour of metals onto AC and IX resins can be attributed to AC's level of activation, particle, and pore size, as well as the activation method (Wu et al., 2009)

Table 15. Statistical parameters of pseudo -first and -second order models, for adsorption of Au and Hg onto Purolite 500Cplus resin at different Au concentrations.

Model	parameter	[Au] ppm			
		1	3	5	7
		Au			
Pseudo first order	K_1	0.002	0.001	0.002	0.0001
	q_e , cal. mg/g	0.045	0.105	0.151	0.370
	q_e , exp. mg/g	0.516	1.421	2.237	3.18
	R^2	0.83	0.46	0.63	0.48
Pseudo second order	K_2	11.39	0.086	0.052	0.029
	q_e , cal. mg/g	0.511	1.495	2.254	3.21
	q_e , exp. mg/g	0.516	1.421	2.237	3.181
	R^2	1	0.9999	1	0.9999
Intraparticle dif. Model	K_{id}	0.002	0.006	0.001	0.017
	R^2	0.576	0.424	0.469	0.458
Hg					
Pseudo first order	K_1	0.002	0.002	0.002	0.002
	q_e , cal. mg/g	0.033	0.028	0.03	0.038
	q_e , exp. mg/g	0.919	0.914	0.844	0.927
	R^2	0.68	0.49	0.48	0.423
Pseudo second order	K_2	0.245	0.254	0.244	0.163
	q_e , cal. mg/g	0.922	0.917	0.848	0.932
	q_e , exp. mg/g	0.919	0.914	0.844	0.927
	R^2	1	1	1	0.9999
Intraparticle dif. Model	K_{id}	0.002	0.002	0.003	0.004
	R^2	0.428	0.365	0.365	0.335

Table 16. Statistical parameters of pseudo -first and -second order models, for absorption of Au and Hg onto AmberSep 91419 resin at different initial Au concentrations.

Model	parameter	[Au] ppm			
		1	3	5	7
Au					
Pseudo first order	K ₁	0.001	0.002	0.002	0.002
	q _e , cal. mg/g	0.035	0.104	0.181	0.274
	q _e , exp. mg/g	0.522	1.43	2.304	3.265
	R ²	0.56	0.58	0.65	0.60
Pseudo second order	K ₂	0.279	0.084	0.0445	0.026
	q _e , cal. mg/g	0.526	1.443	2.323	3.297
	q _e , exp. mg/g	0.522	1.432	2.304	3.265
	R ²	1	1	1	0.9999
Intraparticle dif. Model	K _{id}	0.002	0.006	0.011	0.019
	R ²	0.50	0.455	0.543	0.448
Hg					
Pseudo first order	K ₁	0.003	0.002	0.002	0.002
	q _e , cal. mg/g	0.102	0.076	0.104	0.078
	q _e , exp. mg/g	0.923	0.912	0.842	0.925
	R ²	0.91	0.66	0.70	0.55
Pseudo second order	K ₂	0.097	0.07	0.09137	0.163
	q _e , cal. mg/g	0.931	0.921	0.854	0.937
	q _e , exp. mg/g	0.923	0.912	0.842	0.925
	R ²	1	0.9999	0.9999	0.9998
Intraparticle dif. Model	K _{id}	0.005	0.005	0.006	0.006
	R ²	0.567	0.55	0.618	0.439

Table 17. Statistical parameters of pseudo -first and -second order models, for adsorption of Au and Hg onto activated carbon at different Au concentrations.

Model	parameter	[Au] ppm			
		1	3	5	7
Au					
Pseudo first order	K ₁ , mg/g*min ⁻¹	0.002	0.002	0.002	0.002
	q _e , cal. mg/g	0.683	0.683	0.833	0.826
	q _e , exp. mg/g	0.512	1.449	2.298	3.257
	R ²				
Pseudo second order	K ₂ , mg/g*min ⁻¹	0.027	0.008	0.0048	0.005
	q _e , cal. mg/g	0.54	1.546	2.48	3.427
	q _e , exp. mg/g	0.512	1.45	2.299	3.26
	R ²	0.9992	0.9994	0.9992	0.9989
Intraparticle dif. Model	K _{id}	0.009	0.026	0.0446	0.053
	R ²	0.70	0.791	0.811	0.69
Hg					
Pseudo first order	K ₁ , mg/g*min ⁻¹	0.002	0.002	0.002	0.002
	q _e , cal. mg/g	0.527	0.534	0.481	0.530
	q _e , exp. mg/g	0.688	0.768	0.575	0.625
	R ²	0.98	0.98	0.81	0.98
Pseudo second order	K ₂ , mg/g*min ⁻¹	0.003	0.003	0.006	0.005
	q _e , cal. mg/g	0.795	0.795	0.774	0.737
	q _e , exp. mg/g	0.768	0.768	0.575	0.625
	R ²	0.9974	0.9303	0.9932	0.9738
Intraparticle dif. Model	K _{id}	0.016	0.016	0.018	0.015
	R ²	0.905	0.908	0.871	0.936

Table 18. Statistical parameters of pseudo -first and -second order models, for adsorption of Au and Hg onto Purolite 500Cplus resin at different initial Hg concentrations.

Model	parameter	[Hg] ppm		
		1	4	8
Au				
Pseudo first order	K ₁ , mg/g*min ⁻¹	0.00184	0.00161	0.00184
	q _e , cal. mg/g	0.092	0.12	0.123
	q _e , exp. mg/g	1.487	1.467	1.437
	R ²	0.59	0.58	0.67
Pseudo second order	K ₂ , mg/g*min ⁻¹	0.079	0.064	0.065
	q _e , cal. mg/g	1.488	1.464	1.437
	q _e , exp. mg/g	1.477	1.451	1.424
	R ²	0.9999	0.9999	0.9999
Intraparticle dif. Model	K _{id}	0.007	0.008	0.007
	R ²	0.382	0.444	0.477
Hg				
Pseudo first order	K ₁ , mg/g*min ⁻¹	0.002	0.002	0.001
	q _e , cal. mg/g	0.027	0.13	0.657
	q _e , exp. mg/g	0.543	1.963	3.197
	R ²	0.66	0.68	0.88
Pseudo second order	K ₂ , mg/g*min ⁻¹	0.31	0.059	0.003
	q _e , cal. mg/g	0.543	1.96	3.199
	q _e , exp. mg/g	0.540	1.953	2.991
	R ²	1	0.9999	0.9943
Intraparticle dif. Model	K _{id}	0.0016	0.0075	0.0536
	R ²	0.433	0.389	0.664

Table 19. Statistical parameters of pseudo -first and -second order models, for adsorption of Au and Hg onto AmberSep 91419 resin at different initial Hg concentrations.

Model	parameter	[Hg] ppm		
		1	4	8
Au				
Pseudo first order	K ₁ , mg/g*min ⁻¹	0.002	0.002	0.002
	q _e , cal. mg/g	0.059	0.097	0.146
	q _e , exp. mg/g	1.504	1.487	1.526
	R ²	0.30	0.46	0.57
Pseudo second order	K ₂ , mg/g*min ⁻¹	0.082	0.067	0.05
	q _e , cal. mg/g	1.504	1.487	1.526
	q _e , exp. mg/g	1.492	1.473	1.507
	R ²	0.9998	0.9998	0.9998
Intraparticle dif. Model	K _{id}	0.0078	0.0084	0.0098
	R ²	0.31	0.402	0.466
Hg				
Pseudo first order	K ₁ , mg/g*min ⁻¹	0.002	0.002	0.003
	q _e , cal. mg/g	0.059	0.2564	0.824
	q _e , exp. mg/g	0.543	1.949	2.87
	R ²	0.70	0.70	0.98
Pseudo second order	K ₂ , mg/g*min ⁻¹	0.129	0.028	0.012
	q _e , cal. mg/g	0.543	1.96	2.971
	q _e , exp. mg/g	0.538	1.931	2.862
	R ²	0.9999	0.9999	0.9995
Intraparticle dif. Model	K _{id}	0.003	0.015	0.037
	R ²	0.465	0.538	0.768

Table 20. Statistical parameters of pseudo -first and -second order models, for adsorption of Au and Hg onto activated carbon at different initial Hg concentrations.

Model	parameter	[Hg] ppm		
		1	4	8
Au				
Pseudo first order	K_1 , mg/g*min ⁻¹	0.003	0.003	0.0043
	q_e , cal. mg/g	0.683	0.379	0.377
	q_e , exp. mg/g	1.5	1.48	1.51
	R^2	0.73	0.73	0.78
Pseudo second order	K_2 , mg/g*min ⁻¹	0.011	0.012	0.014
	q_e , cal. mg/g	1.569	1.544	1.57
	q_e , exp. mg/g	1.492	1.473	1.507
	R^2	0.9981	0.998	0.9984
Intraparticle dif. Model	K_{id}	0.024	0.023	0.022
	R^2	0.644	0.611	0.571
Hg				
Pseudo first order	K_1 , mg/g*min ⁻¹	0.002	0.003	0.003
	q_e , cal. mg/g	0.215	0.684	0.513
	q_e , exp. mg/g	0.429	1.514	2.339
	R^2	0.95	0.97	0.95
Pseudo second order	K_2 , mg/g*min ⁻¹	0.024	0.01	0.003
	q_e , cal. mg/g	0.449	1.580	2.536
	q_e , exp. mg/g	0.422	1.507	2.339
	R^2	0.9991	0.9998	0.9962
Intraparticle dif. Model	K_{id}	0.007	0.023	0.048
	R^2	0.825	0.807	0.881

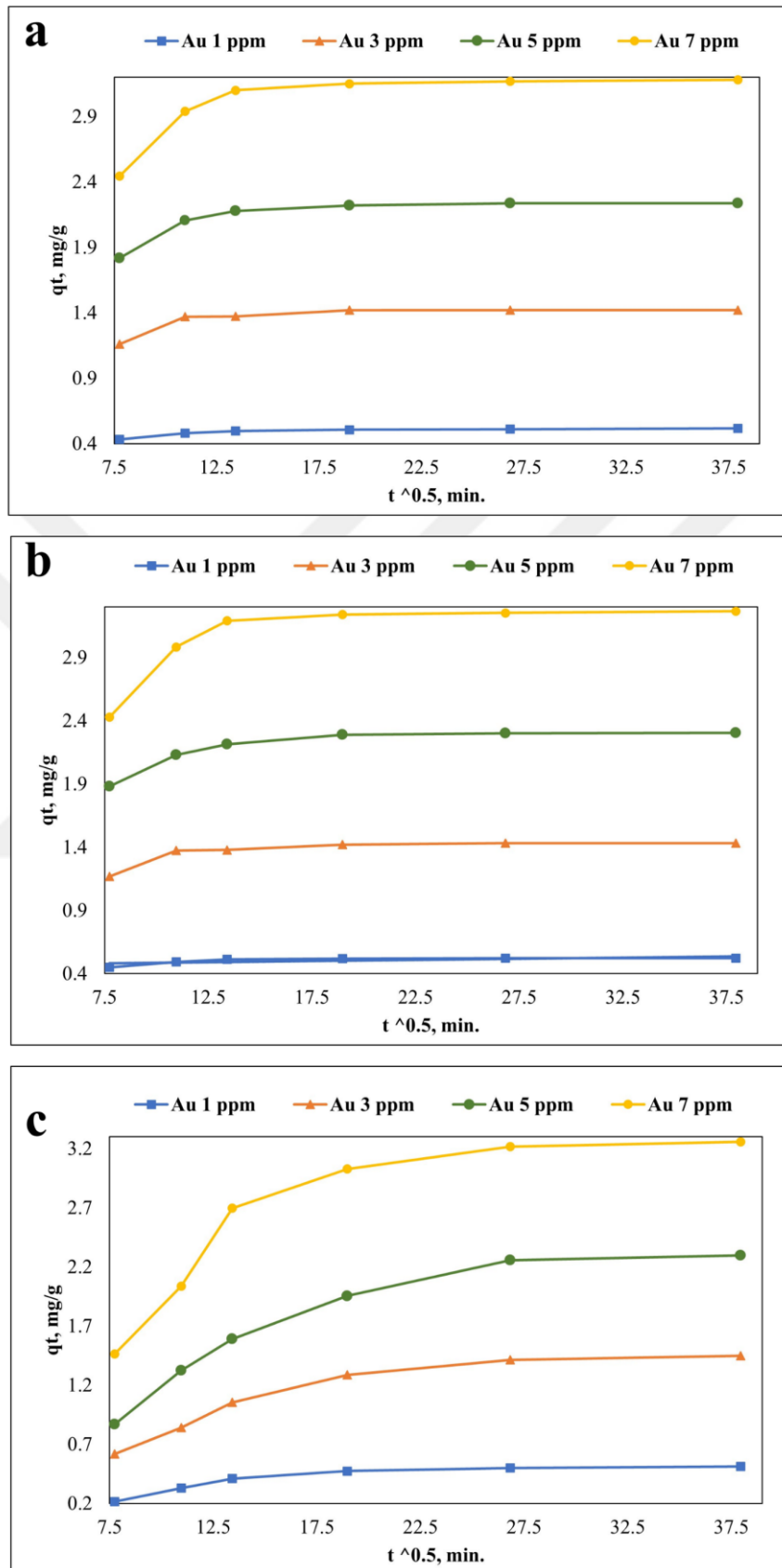


Figure 27. Fitting the data of Au adsorption onto, Purolite A500 CPlus(a), AmberSep M91419 (b) and AC (c) to IPD model.

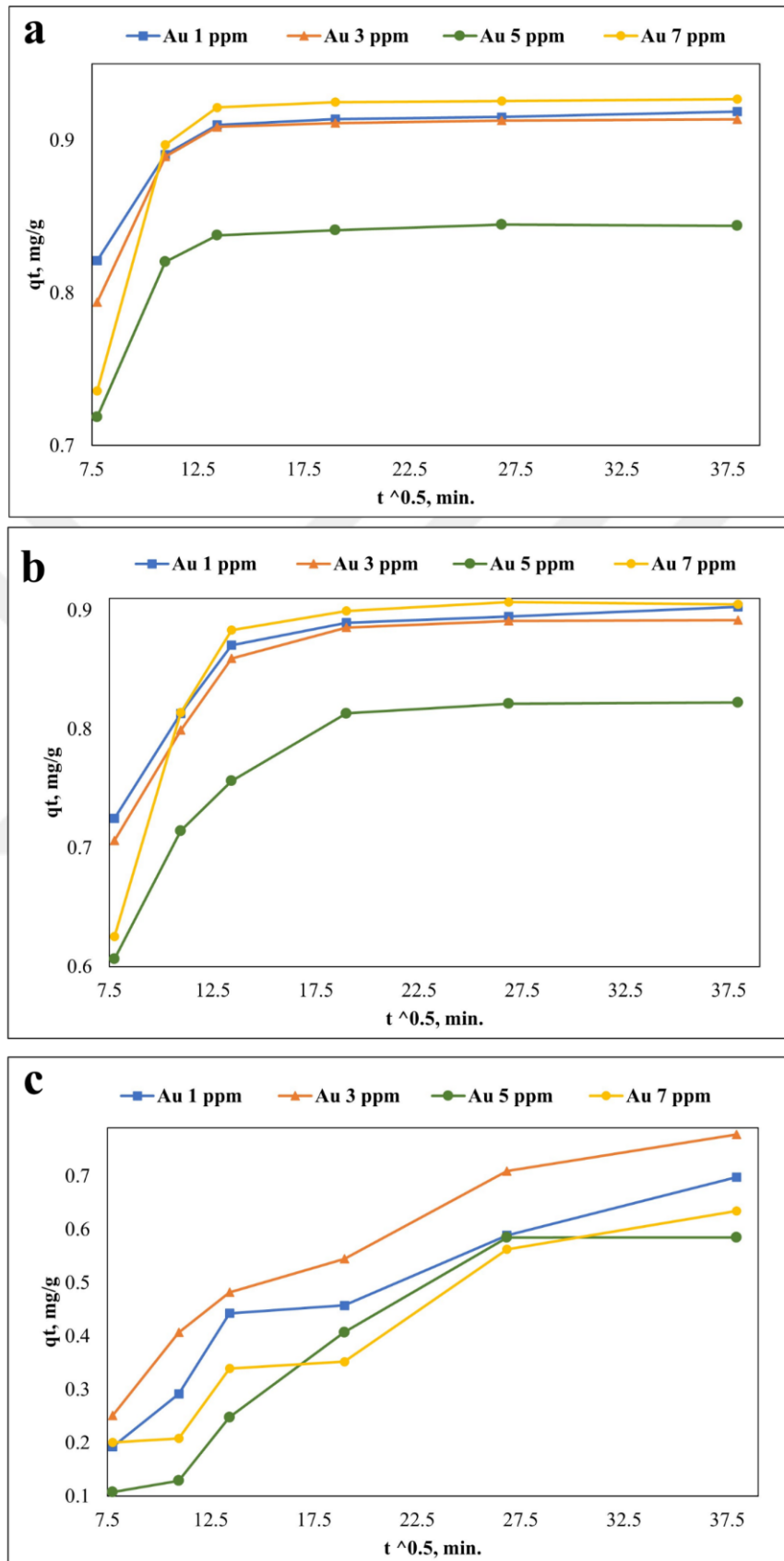


Figure 28. Fitting the data of Hg adsorption onto, Purolite A500 CPlus(a), AmberSep 91419 (b) and AC (c) to IPD model.

4.2.7. Adsorption Isotherms

The adsorption data of Au onto IX resins and GOLD was analysed using Langmuir (LAIM) and Freundlich adsorption isotherm models (FAIM), as it is presented in Figure (29). The parameters of both models were calculated from the fitted data, as shown in Table 21. The evaluation of the models was based on the regression correlation coefficients R^2 . It was observed that the R^2 values of FAIM (0.9989 and 0.9983) were slightly higher than those obtained by LAIM (0.9952 and 0.9966) for Purolite 500CPlus and AmberSep 91419, respectively. These results are consistent with the findings of Deng, et al. (2020), who studied the recovery of gold from cyanide-starved glycine solutions in the presence of Cu using a molecularly imprinted resin (IXOS). They also concluded that fitting the data to FAIM does not necessarily indicate that the Freundlich mechanism is dominant, but rather suggests that the parameters estimated by Freundlich are more accurate. However, the data fitting to FAIM suggests that the adsorption is non-ideal, multilayer, and reversible. Another common observation is that the value of $1/n$ obtained by LAIM for the adsorbents is $0 < 1/n < 1$, indicating favourable adsorption (Al-Ghouti & Da'ana, 2020).

Table 21. Langmuir and Freundlich adsorption isotherm parameters for Au adsorption onto different adsorbents

Adsorbent	Isotherm model					
	Langmuir			Freundlich		
	K_L	q_m	R^2	K_F	n	R^2
Purolite 500CPlus	0.06085	26.95	0.9952	1.826	1.366	0.9989
AmberSep 91419	0.08179	20.9	0.9966	1.891	1.487	0.9983
Activated Carbon	0.01046	43.61	0.9929	0.485	1.092	0.9906

In the case of the adsorption of Au onto activated carbon, the Langmuir model provided a better fit to the data compared to the Freundlich model. The coefficient of determination (R^2) for the Langmuir model was 0.993, which is relatively higher than the R^2 value of 0.9906 obtained for the Freundlich model. These findings are consistent with the results reported by Tauetsile, et al. (2018) in their study on the adsorption behaviour of Au

and Cu-glycinates onto activated carbon using the Freundlich model. Where, the highest R^2 value obtained for the Freundlich model was in agreement with the value obtained in this current study.

Furthermore, the adsorption intensity values ($1/n$) observed in the aforementioned study were all greater than 1, indicating unfavourable adsorption conditions. This raises questions about the suitability of the Freundlich model for fitting the data, suggesting that the Langmuir model would have provided a better fit. In this current study, according to the Langmuir adsorption isotherm model (LAIM), the process of Au adsorption onto AC was found to be homogeneous and monolayered. Additionally, the calculated value of R_L (0.905) from the Equation (17) indicates that the adsorption process is favourable.

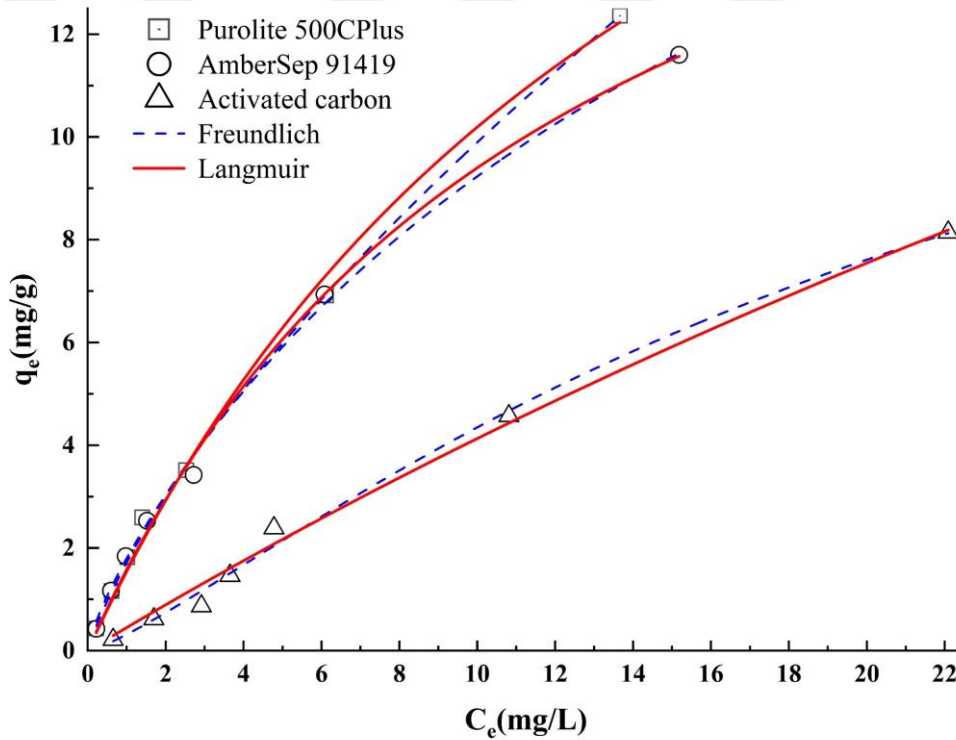


Figure 29. Langmuir and Freundlich isotherms of Au adsorption onto different adsorbents.

4.3. Elution Experiments Results

After the successful optimization of the adsorption process and the achievement of satisfactory adsorption rates, various methods such as adsorption kinetics, isotherm models, and instrumental analysis were employed to interpret the results. Subsequently, numerous

experiments were conducted to achieve the selective elution of the adsorbed metals from the adsorbent. In this particular section, preliminary tests were conducted to identify the appropriate eluent for both Au and Hg. Once the eluents were selected, the impact of several factors on the elution process was investigated, and the findings were presented and discussed. Furthermore, the elution kinetics of both Au and Hg were examined, along with cycle tests to evaluate the durability of the adsorbents, based on the optimal conditions determined from the aforementioned experiments.

4.3.1. Mercury Elution Pre-Tests

The effectiveness of three different acids, HNO_3 , H_2SO_4 , and HCl , in removing mercury from IX resins and AC loaded with Au, Ag, Cu, and Hg was assessed in preliminary elution tests. These tests involved using 40 bed volumes (BV) of 2M acid at room temperature for four hours. The results of these tests are shown in Figure 30.

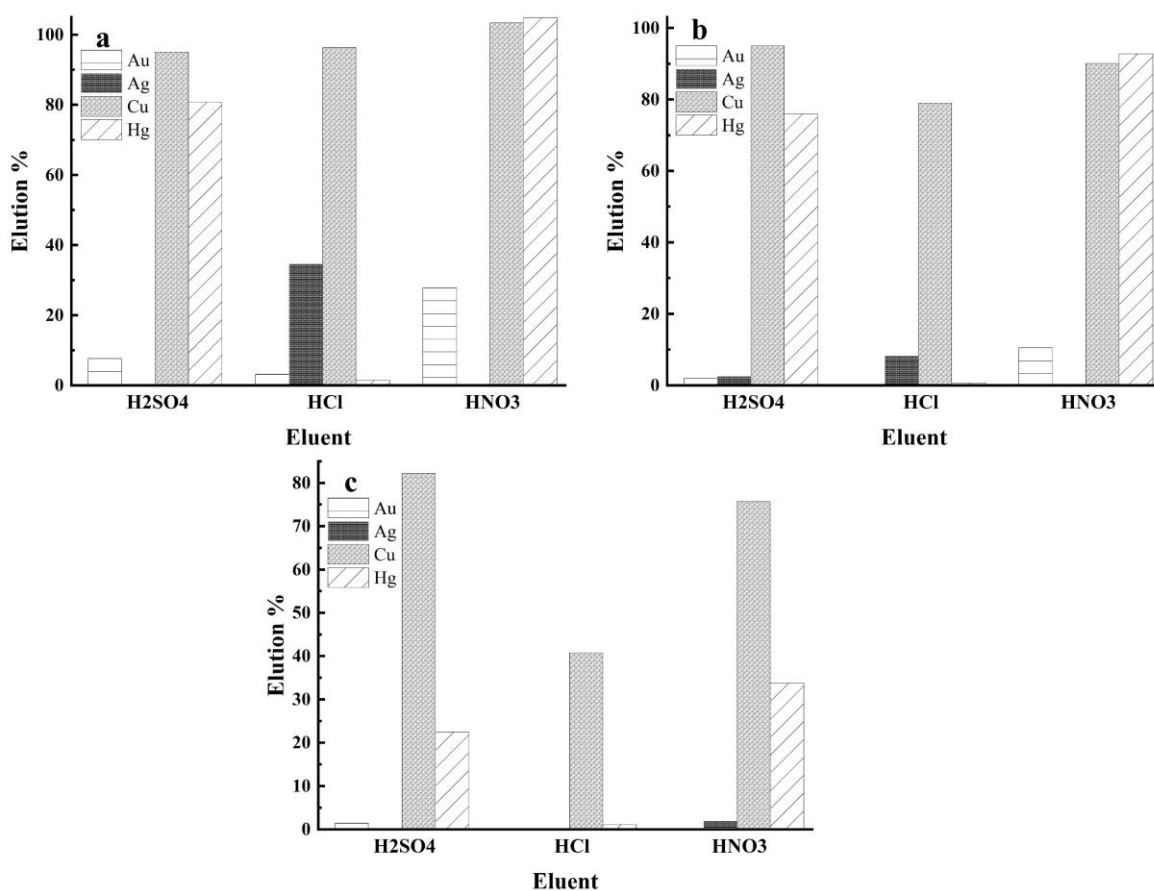


Figure 30. Elution pre-tests of Hg from Purolite 500CPlus (a), AmberSep 91419 (b) and Activated Carbon (c).

Both sulfuric acid and nitric acid were able to remove both Hg and Cu from the resins. However, nitric acid performed better than sulfuric acid in elution of Hg and Cu. When nitric acid was used, 100% of Cu and 90% of Hg were successfully removed from Purolite 500CPlus, while 100% of Cu and 92% of Hg were removed from AmberSep 91419. On the other hand, sulfuric acid resulted in the removal of 95% of Cu and 80% of Hg from Purolite 500CPlus, and 95% of Cu and 75% of Hg from AmberSep 91419.

Despite advantageous of using nitric acid on mercury removal, it was less selective towards Au when compared to sulfuric acid. When sulfuric acid was used, only 7% and 2% of Au were removed from Purolite 500CPlus and AmberSep 91419 resins, respectively. In contrast, nitric acid led to the removal of more than 27% and 10% of Au from Purolite 500CPlus and AmberSep 91419 resins, respectively. This significant amount of gold eluted, along with mercury, is considered unacceptable as it can result in gold losses during the downstream mercury recovery processes.

In terms of its performance, hydrochloric acid yielded satisfactory results in the elution of Cu, but it was unable to remove Hg from either of the adsorbents. The effectiveness of sulfuric acid and nitric acid in mercury elution can be explained by the instability of the complexes formed between Hg and these acids. According to Baba, et al. (2006), the stability of these complexes can be arranged in ascending order as $\text{Hg(II) di-halides} > \text{Hg(SO}_4)_2^{2-} > \text{Hg-nitrate}$ (Baba et al., 2006). This finding aligns with the results reported by Atia, et al. (2005), who investigated the separation of mercury using chelating resin. They observed that the elution rates achieved using HNO_3 , H_2SO_4 and HCl were 90%, 94%, and 32% respectively. The higher efficiency of H_2SO_4 could be attributed to the characteristics of the resin employed in that particular study.

During the stage of AC elution, the elution of Cu was deemed satisfactory. However, the solutions used were not successful in eluting of Hg. HNO_3 and H_2SO_4 were able to elute 33% and 22% of Hg respectively, while hydrochloric acid HCl only achieved 1% elution. The low elution of Hg using HCl can be attributed to the formation of the highly adsorbable HgCl_3^- complex at high acid concentration (Atia et al. 2005). The challenge of removing Hg from AC, even with high acid concentrations, suggests that elevated temperatures may be necessary to achieve satisfactory Hg elution. However, this approach is more energy-intensive and environmentally unfriendly, making AC an unfavourable option to pursue. Since HCl has proven inadequate for eluting mercury from both IX resins and AC, a decision must be made regarding the remaining eluents. Despite its efficiency as a Hg eluent, the

higher cost and poor selectivity of HNO_3 towards Au make H_2SO_4 a better choice for mercury elution from IX resins.

4.4. Effect of Parameters on Mercury Elution

The study aimed to investigate the impact of various factors, including eluent concentration, bed volume, elution time, and temperature, on the elution of mercury from Purolite 500CPlus and AmberSep 91419 resins. The main objective was to identify the optimal conditions that would minimize the elution of gold while maximizing the elution of mercury. To achieve this, the experiments were conducted under the preliminary test conditions. A systematic approach of altering one parameter at a time was employed to observe the individual effects of these parameters was applied.

4.4.1. Effect of Eluent Concentration

Staker and Sandberg (1987) conducted a study on the selective elution of Au, Ag, and Hg. They found that using 0.1M - 1M of H_2SO_4 , up to 95 - 98% of Hg can be eluted from IRA-430 resin loaded with $\text{Hg}(\text{CN})_2$. In this current study, the effect of H_2SO_4 concentration on mercury elution from Purolite 500CPlus and AmberSep 91419 resins was investigated, as shown in Figure 31 .

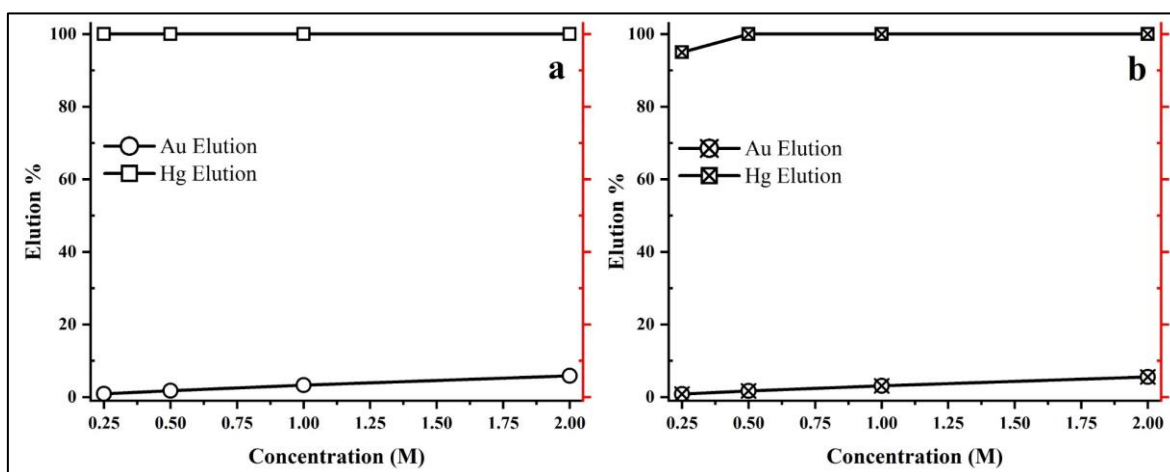


Figure 31. Effect of sulfuric acid concentration on Au and Hg elution from Purolite 500Cplus (a) and AmberSep 91419 (b), at 40 BV, retention time 4 hours, temperature 25 °C and shaking speed 200 rpm.

It was observed that only 0.25M of the acid was sufficient to completely elute Hg from Purolite 500CPlus. On the other hand, 0.5M of the eluent was required to achieve desorption from AmberSep 91419 resin. Atia, et al. (2005) used 6M of H_2SO_4 to elute 94% of Hg from a synthesized chelating resin loaded with HgCl_2 . The need for a more concentrated eluent in their study compared to the current one can be attributed to the nature of the resin and the stability of the solution used in the loading of the resins.

When it comes to the elution of Au from the resins, the amount of Au eluted at 0.25 M H_2SO_4 was 0.91% for Purolite 500CPlus and 0.67% for AmberSep 91419. These percentages increased incrementally to reach 5.58% and 5.56% respectively when the concentration of H_2SO_4 was increased to 2M. According to Staker and Sandberg (1987), the aurocyanate complex is not soluble in diluted acids. Therefore, when Au is eluted with Hg, it can be easily filtered from the elution solution. This finding can be extrapolated to Au-glycinate complexes based on the similarity between $\text{Au}(\text{CN})_2^-$ and $\text{Au}(\text{Gly})_2^-$. To maximize the elution of Hg while minimizing the elution of Au, it is recommended to use a 40 BV (bed volume) of 0.5 M H_2SO_4 solution. This choice is considered the most viable option based on the research findings.

4.4.2. Effect of Bed Volume

In a study conducted by Atia, et al. (2005), the researchers examined the release of mercury from the synthesized resin by using different concentrations of H_2SO_4 . The findings indicated that the percentage of elution increased as the amount of eluent was increased up to a certain point. The most favourable outcomes were obtained when using 40 ml (400 BV) of 6 M H_2SO_4 . It is worth noting that the quantity of solutions used in this study was significantly higher compared to previous research data.

In current research, the impact of BV volume on the elution of Hg and Au was investigated. The results presented in Figure (32) demonstrated that 20 BV of the eluent was insufficient to remove mercury from either of the resins. However, 3.3% and 3% of Au were eluted from Purolite 500CPlus and AmberSep 91419, respectively. Increasing the eluent volume to 30 BV resulted in complete removal of Hg from both resins, but it also led to an increase in Au elution to 4.5% and 4.3% from both resins. Which continued to rise with increasing BV, reaching 6.8% and 6.4% at 50 BV. In an effort to use 30 BV of the eluent in the further experiments, additional experiments were conducted using 30 BV of 0.25 and 0.5

M H_2SO_4 solution. The maximum achieved result was an 80% Hg elution, indicating the significant role of BV in the elution process. Consequently, a BV of 40 was selected for further investigations.

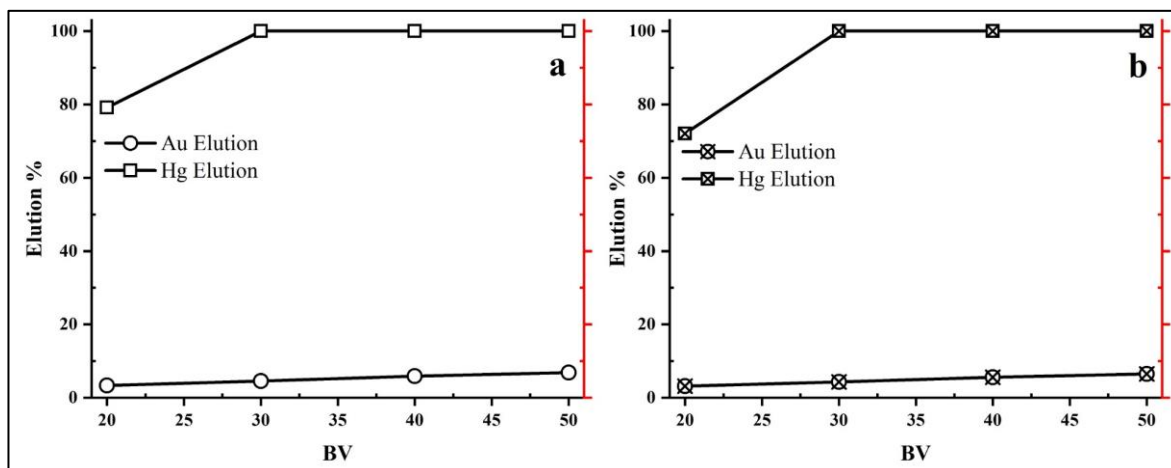


Figure 32. Effect of eluent amount (BV) on Hg and Au elution from Purolite 500Cplus (a) and AmberSep 91419 (b), at eluent concentration 2 M, retention time 4 hours, temperature 25 °C and shaking speed 200 rpm.

The importance of BV becomes evident when considering the fact that even though the concentration of eluent was sufficient to effectively remove the Hg from the resin, using smaller BV leads to a high concentration of the desorbed metal in the solution. As a result, this high concentration forces the reaction to shift towards the left and adsorb again onto the resin.

4.4.3. Effect of Retention Time

Elution rates may vary depending on the volume and concentration of the eluent. Consequently, the process may be completed in a shorter or longer period of time. To examine the effect of time on elution, a series of experiments were conducted within a time range of 2 to 8 hours. The results, illustrated in the associated Figure 33, indicated that a duration of 2 hours was insufficient to completely remove Hg from either of the resins. Purolite 500CPlus and AmberSep 91419 exhibited elution percentages of 85.3% and 79.3% respectively. However, complete elution of both resins was achieved after 4 hours.

In a study conducted previously by Berg and Truemper (1958) on the separation of Zinc, Cadmium, and Mercury using Dowex-1 X 10 ion exchange resin, it was reported that

a complete mercury elution could be accomplished within a mere two hours using a mixture of 0.1M thiourea and 0.01M hydrochloric acid. Another study by De Wuilloud (2002) found that it only took 14 minutes to elute mercury from Dowex 1X-8 anion exchange resin using 3 M of HNO_3 . This rapid elution was attributed to the nature of the organic mercury complex used to load the resin, which can be easily stripped.

Interestingly, while the elution percentage of Hg remained constant after the fourth hour, the elution of Au showed a slight increase over time. At 6 hours, the elution percentages of Au from Purolite 500Cplus and AmberSep 91419 were 7.5% and 7% respectively, before decreasing to 6.6% and 6.2% at 8 hours. Notably, the values of Au desorption from both resins at 2- and 4-hour retention times were nearly identical, suggesting that extending the elution time to four hours could result in better Hg elution without affecting Au.

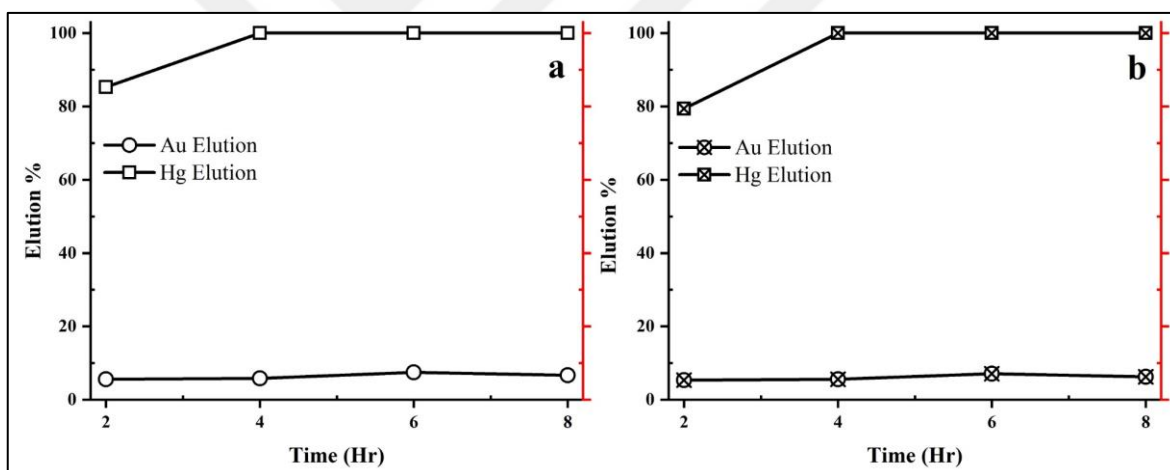


Figure 33. Effect of retention time on Hg elution from Purolite 500Cplus (a) and AmberSep 91419 (b), at eluent concentration 2 M, 40 BV, temperature 25 °C and shaking speed 200 rpm.

4.4.4. Effect of Temperature

The elution process is commonly known to be endothermic, indicating that an increase in temperature leads to an enhancement in elution. Staker and Sandberg (1987) successfully achieved a 95% elution of Hg by employing 0.1M of H_2SO_4 . In this specific research, although a complete elution of Hg was attained at room temperature, the impact of temperature on other metals was examined, considering the potential application of the

process in regions with high temperatures. Figure 34 demonstrates the influence of temperature on the elution of Hg and Au within the temperature range of 25-55 °C. Interestingly, the elution of Hg remained unaffected by the elevation of the temperature, while the elution of Au increased to 12.2% and 11.46% for Purolite 500CPlus and AmberSep 91419, respectively, before decreasing to 10% and 9.31% when the temperature reached 55°C. This decrease in Au elution can be attributed to the maximum operating temperature of the resin in the chloride form, which is 60°C, expected to be lower than that in an acidic environment.

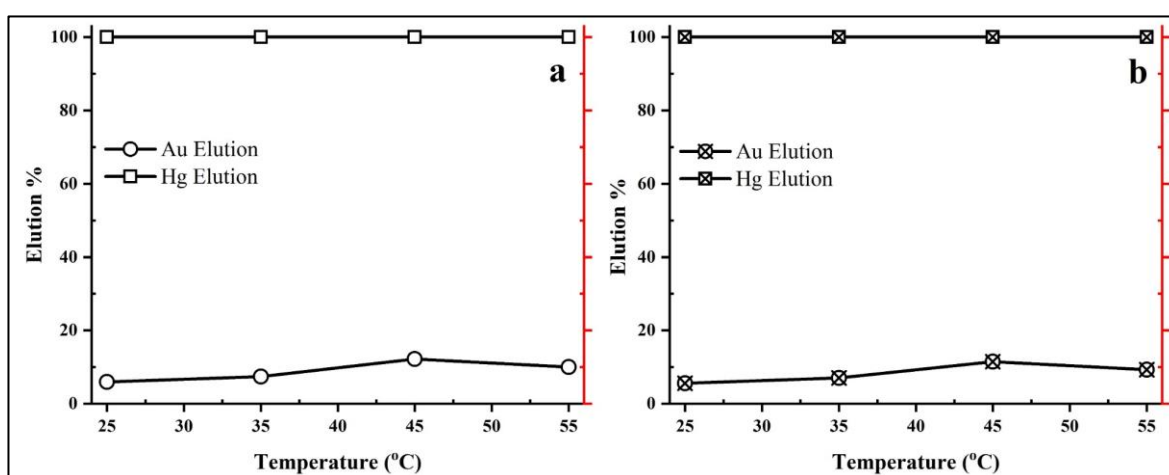


Figure 34. Effect of temperature on Hg and Au elution from Purolite 500Cplus (a) and AmberSep 91419 (b), at eluent concentration 2 M, 40 BV, retention time 4 hours and shaking speed 200 rpm.

As a suggested solution, if the utilization of temperatures higher than 25°C is unavoidable, it is recommended to employ a smaller quantity of low-concentration solution to achieve the desired Hg elution while minimizing Au elution.

4.4.5. Kinetics of Mercury Elution

In previous experiments, the optimal conditions for the Hg elution process were determined to be an eluent concentration of 0.5 M, an eluent amount of 40 BV, a retention time of 4 hours, a temperature of 25°C, and a shaking speed of 200 rpm. By implementing these conditions, the elution profile of Hg from IX resins was observed within a 4-hour time frame. Figure 35 depicts the desorption kinetics of Hg from Purolite 500Cplus and AmberSep 91419 resins. It is evident that the desorption of Hg from Purolite 500Cplus

occurred at a faster rate compared to AmberSep 91419. Within the initial 15 minutes, approximately 45% of Hg was desorbed from Purolite 500Cplus, while approximately 40% was stripped from AmberSep 91419. This trend persisted until the third hour of the elution process. Subsequently, the elution kinetics of Purolite 500Cplus gradually slowed down, whereas the elution of AmberSep 91419 continued to incrementally increase. As a result, the respective elution percentages reached 96% for Purolite 500Cplus and 94.5% for AmberSep 91419.

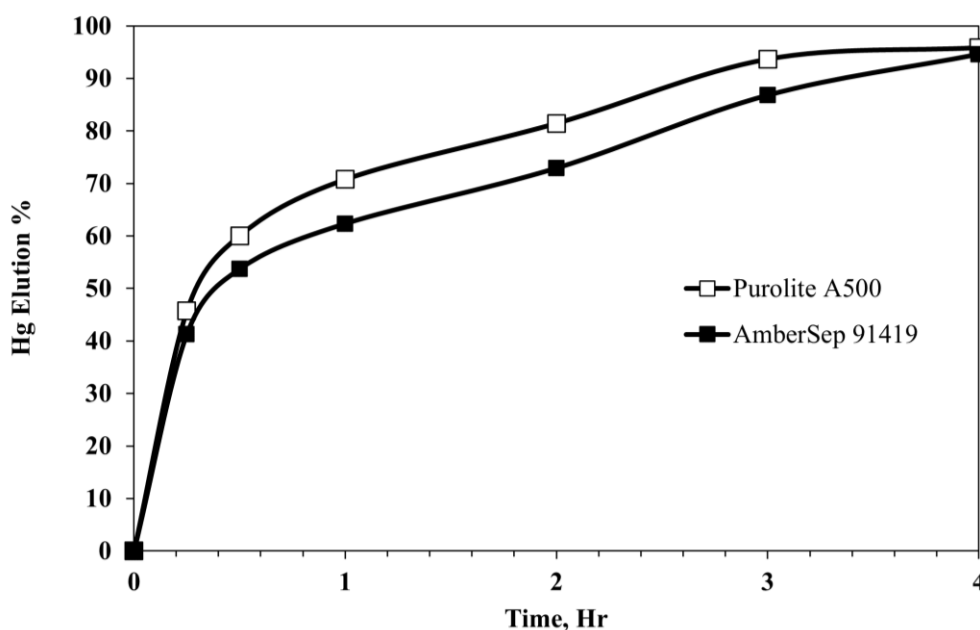


Figure 35. Kinetics of Hg elution from Purolite 500Cplus and AmberSep 91419, eluent concentration 0.5 M, 40 BV, temperature of 25 °C, and a shaking speed of 200 rpm.

4.5. Gold Elution Pre-Tests

Following the successful optimization of the mercury elution process, additional preliminary tests were carried out to identify a suitable eluent for gold. Four different eluent solutions were tested. The first eluent consisted of a mixture of 0.75% v/v NaOCl, 150g/l NaCl and 5g/l NaOH. The second eluent was 2M NaClO₄, the third eluent was a combination of NaClO₄ and 10 g/l of NaOH and the fourth eluent was well-known acidic thiourea with 2M H₂SO₄ and 2M thiourea. The process conditions were, shaking speed of 200rpm and a temperature of 40 °C and eluent volume of 40 BV, As depicted in Figure 36. It was observed

that the acidic thiourea solution demonstrated the most favourable performance among the four eluents. It achieved an Au elution of 98.5% and 94%, as well as an Ag elution of 94% and 64% from Purolite A500Cplus and AmberSep 91419 resins, respectively. However, despite its effectiveness and regenerative properties (Adams, 2005), the acidic thiourea elution process is highly corrosive. This can lead to significant damage to the electrowinning cell's structure and, more importantly, cause degradation of the resin due to osmotic shock (Marsden & House, 2006). In order to avoid this concern, the alternative eluents containing NaCl and NaOH were considered. This is because both resins are manufactured with active sites in the form of Cl^- or OH^- . Additionally, the weak adsorption of chloride onto the resins makes them ideal ion exchangers for Au without the need for further regeneration (Jeffrey et al., 2010).

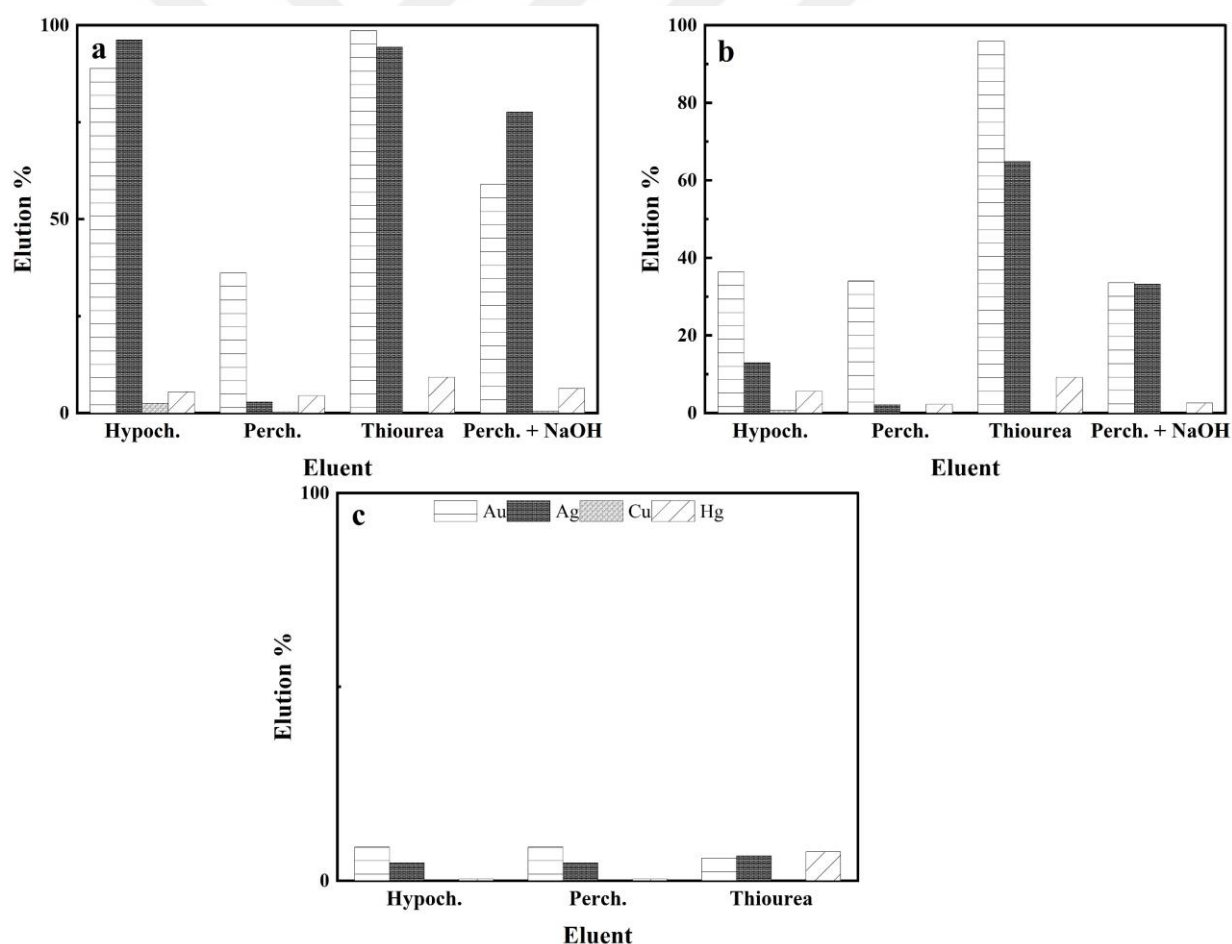


Figure 36. Elution pre-tests of Au and Hg from Purolite 500CPlus (a), AmberSep 91419 (b) and Activated Carbon (c).

4.6. Parameters Effect on Gold Elution

Based on the outcomes of the eluents screening tests, the solution comprising of NaClO, NaOH, and NaCl has been chosen as the Au eluent from both Purolite A500CPlus and AmberSep 91419 resins. The elution of strong IX resin is influenced by various factors, including the concentration of the eluent and the temperature (Marsden & House, 2006). Furthermore, the eluent volume and the elution time are crucial aspects of the elution process. Considering these factors, the impact of NaClO and sodium chloride (NaCl) concentration, as well as the bed volume, retention time, and temperature on Au elution, were investigated.

4.6.1. Effect of Sodium Chloride Concentration

Jeffrey, et al. (2010) successfully achieved a complete elution of Au-thiosulfate from (Purolite A500/2788) IX resin using a mixture of 2 M NaCl and 0.1 M Na₂SO₃. On the other hand, Rajasingam, et al. (2006) investigated the impact of counterions, such as OH⁻, Cl⁻ and CN⁻, on the elution of aurocyanate complex from the same resin using *N*-methyl-2-pyrrolidone and water. Their findings indicated that Cl⁻ was the second most effective among the three counterions. In this study, the researchers examined the effect of NaCl concentration in the range of 50 - 200 g/l on the elution of Au from Purolite A500CPlus and AmberSep 91419 resins. An eluent containing 0.75% NaClO and 5 g/l NaOH was used. The results, as shown in the Figure 37, indicate that increasing the concentration of Cl⁻ did not significantly impact Au elution from Purolite A500CPlus. However, it noticeably affected Ag elution, with an increase of approximately 20% when the NaCl concentration was increased from 50 g/l to 200 g/l. In the case of AmberSep 91419, both Au and Ag elution exhibited a similar response to increasing NaCl concentration. Increasing the dosage of NaCl from 50 g/l to 200 g/l resulted in a total gradual increase in both Au and Ag elution by 10%. It can also be noticed that increasing the concentration of NaCl beyond 150 g/l did not result in any significant result except for the elution of Ag from Purolite 500CPlus, this can be attributed to the increase of the viscosity of the solution which result in a slower diffusion of the solution through the resin.

Rajasingam, et al. (2006) highlighted that the utilization of chloride ions (Cl⁻) in a mixed solution plays a crucial role in enhancing the elution process through the formation of metal chloro-complexes. This finding is consistent with the earlier work of Fleming and

Monhemius (1979). The relatively lower elution of silver compared to gold can be attributed to the larger ionic radius of Ag, resulting in the formation of a larger complex with lower charge density compared to the Au complex; (charge density = charge/ionic radius). This lower charge density causes Ag to be less hydrated and more inclined to remain bound to the solid phase. This claim can be supported by the example of gold thiosulfate complex $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ which due to its high hydrophilicity does adsorb onto activated carbon (Oliveira, et al., 2008). Over all, based on the results obtained from this very study, the optimal concentration of NaCl for achieving the highest elution of precious metals was 150g/l.

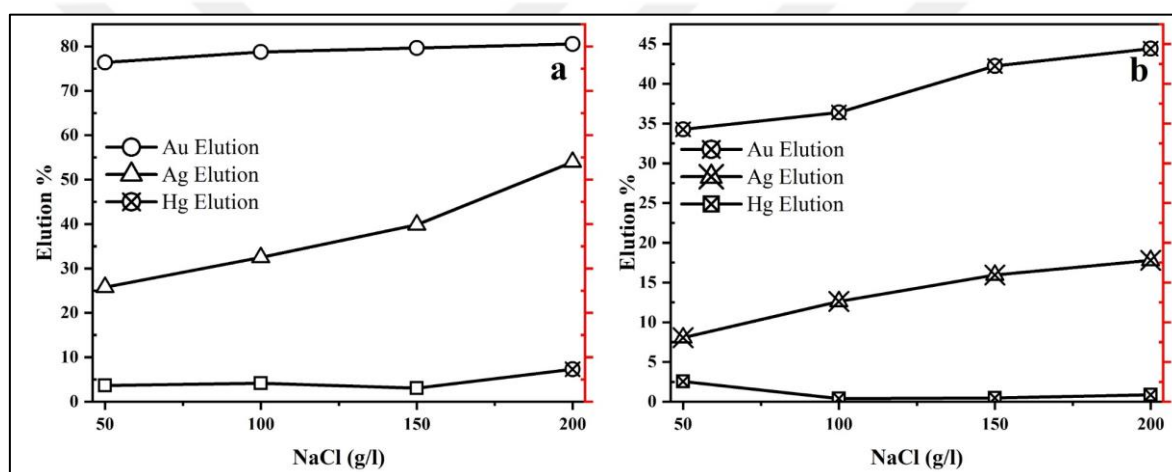


Figure 37. Effect of NaCl concentration on elution of Purolite 500Cplus (a) and AmberSep 91419 (b), at NaClO .75%, NaOH 5 g/l, 40 BV, retention time 12 hours, temperature 40 °C and shaking speed 200 rpm.

4.6.2. Effect of Sodium Hypochlorite Concentration

The decision to incorporate sodium hypochlorite into the elution mixer was made based on various studies conducted by many researchers. Radulescu (2008) conducted a study on the use of Chlorine, which is generated from the reaction between NaClO and HCl, to extract gold from secondary sources of gold. Staker and Sandberg (1987) were successful in achieving an 89% Au elution from IRA-900 resin loaded with Au-cyanide complex using a mixer consisting of NaClO, NaCl, and NaOH. In order to assess the impact of NaClO on the elution of Au in this study, Purolite A500CPlus and AmberSep 91419 resins loaded with Au- and Ag-glycinate were eluted with solutions containing 0.25% - 1% v/v NaClO.

The experimental results depicted in Figure 38 indicate that the concentration of NaClO has a positive impact on the elution of Au from both Purolite A500CPlus and AmberSep 91419 resins. Specifically, increasing the concentration from 0.25% to 1% led to an increase in Au elution from 60% to 89% and from 29% to 51% for both resins, respectively. However, the same increase in NaClO concentration did not significantly enhance Ag elution. Instead, Ag elution only increased by 7% from both resins, reaching 41% and 15.26% for both resins, respectively. Interestingly, a slight decrease in Ag elution from Purolite A500CPlus was observed when the NaClO concentration increased from 0.75% to 1%, although the reason for this decrease remains unclear.

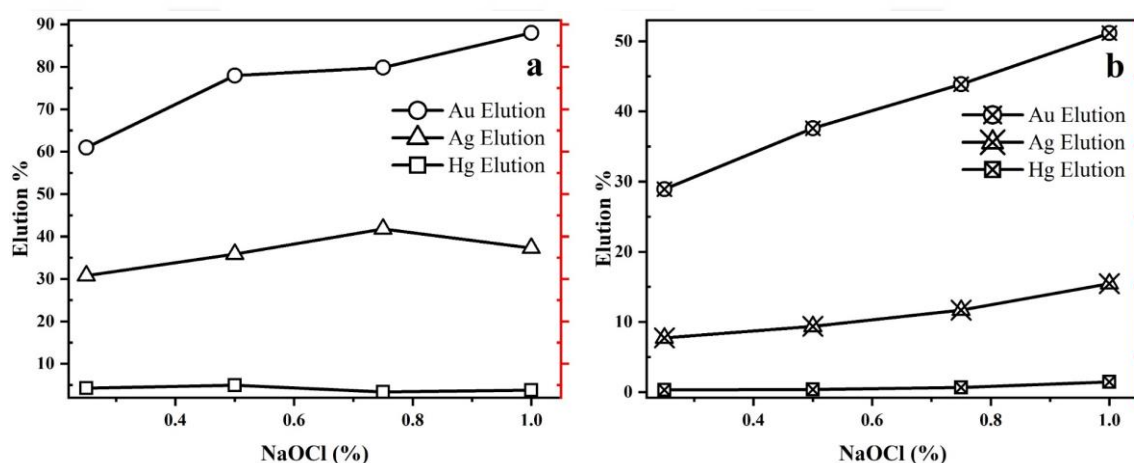


Figure 38. Effect of NaClO concentration on elution of Purolite 500Cplus (a) and AmberSep 91419 (b), at NaCl 150 g/l, NaOH 5 g/l, 40 BV, retention time 12 hours, temperature 40 °C and shaking speed 200 rpm.

There is a lack of research on the elution of Au and Ag from IX resin using hypochlorite, and the only available study does not provide information on the effect of parameters on the elution process or the mechanism of elution. Baghalha (2007) conducted a study on the dissolution of gold from oxide ores using chloride/hypochlorite solutions with chlorine as an oxidant in an acidic medium. Equation (32) shows the mechanism of the reaction. The same principle can be applied for the elution of gold from resin in alkaline media using oxygen of hypochlorite as an oxidant. According to the findings of this investigation, it was observed that the concentration of NaClO had a significant impact on the elution of Au from both resins. The highest percentage of Au achieved was obtained when the NaClO concentration was 1% v/v. However, it should be noted that at this concentration, there was a slight decrease in the elution of Ag from Purolite 500Cplus.



4.6.3. Effect of Eluent Bed Volume

Bed volume (BV) is an important factor in elution experiments; most of the studies focus on the optimization of the process parameters' effect are taking it in consideration. In a study conducted by Oliveira, et al. (2008) to elute gold cyan-complex from Bayer AP-247 and Purolite A500 resin using nitrate and thiocyanate solutions, they found that 8BV of 1 M NaNO_3 was enough to elute 90% of the gold from Bayer AP-247 resin while 20 BV of the same solution eluted less than 10% Au from Purolite A500 resin. only 5 BV of 1M NaSCN resulted in 88% Au elution from AP-247 resin, but it required 20 BV of the solution to elute the same amount of Au from Purolite 500. The elution of Au from minix (AmberSep 91419) resin loaded with Au-cyanide complex was investigated by Schoeman, et al. (2013). They found that using 20 BV of 2M of KSCN solution resulted in 83% Au elution. The findings stated clearly show the difficulty of Au elution from AmberSep as compared to Purolite 500 resin even with more concentrated solution, which explains the high affinity of AmberSep 91419 towards Au.

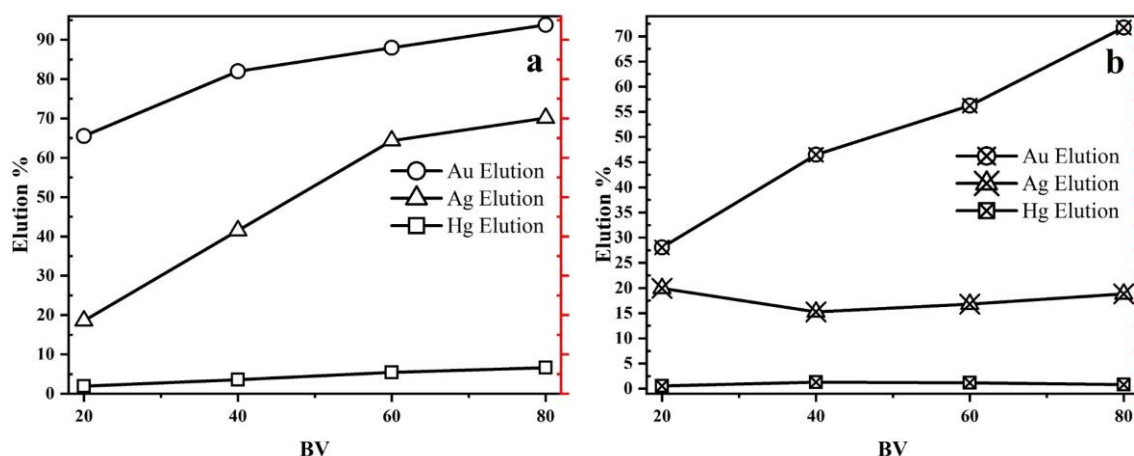


Figure 39. Effect of eluent bed volume on elution of Purolite 500Cplus (a) and AmberSep 91419 (b), at NaCl 150 g/l, NaOH 5 g/l, NaClO 0.75%, retention time 12 hours, temperature 40 °C and shaking speed 200 rpm.

In this study the effect of the eluent BV on Au from both resins was experimented. As it is presented in Figure 39, the increase of the bed volume yielded a positively incremental on Au and Ag elution from Purolite 500CPlus resin; the elution of Au and Ag increased

gradually from 65% and 18.5% to reach 94% and 71% respectively. However, the increase of the BV had a positive effect on the elution of Au from AmberSep 91419, it did not lead to any improvement in Ag elution. While Au elution escalated from 28% to 71% the Ag's remained unceasingly fluctuated between 19% and 15%. Using 40 BV of the same solution Staker and Sandberg (1987), have achieved Au elution ranged between 93% - 98% from different strong base IX resins loaded with Au-cyanide complex within 9 hours. The reason why the elution of the Au-cyanide from IX resins is easier than that of Au-glycine is the low charge density; although both anions have the same charge Au-glycine complex possess a larger ionic radius which renders it less charged and resultantly more hydrophobic (Rajasingam et al., 2006; Oliveira et al., 2008). As in the case of using thiocyanate for Au elution discussed in the above paragraph, it is interesting that AmberSep 91419 showed the same lower elution as compared to Purolite 500CPlus.

This can be explained by the high affinity of AmberSep towards gold which is a bit difficult using a basic solution. However, using acidic solution Au can easily be eluted from it, as has been reported by Schoeman (2013) who achieved an elution of 100 using only 15 BV of a solution containing 0.5M thiourea and 0.5 M HCl. While in the basic solution even with the well-known eluents. Using 25 BV of 2M KSCN and 0.5 M of $\text{Zn}(\text{CN})_4^{2-}$ solutions to elute aurocyanide from AmberSep 91419 at 22 and 50 °C, Schoeman (2017) achieved about 80% and 18%, respectively. They attributed the difficulty of this resin elution to the tri-butyl function groups.

The significance of the eluent BV in the process is explicitly emphasized by these findings. As previously indicated in this study, a decrease in bed volume results in an increase in metal concentration within the eluent, leading to re-adsorption of metals. To counteract this phenomenon, it is necessary to employ a larger BV to attain effective elution of Au and Ag. it is recommended to utilize 80 BV.

4.6.4. Effect of Retention Time

In their study on the elution of Au from Purolite 500, Rajasingam, et al. (2006) reported that it took 8 hours for the elution process to reach equilibrium. On the other hand, Staker and Sandberg (1987) conducted a preliminary test to examine the possibility of Au-cyanide elution from IRA-900 resin using an eluent similar to the one used in this, and it took 10 hours of contact time to elute 92% of Au. Another experiment was carried out using

AmberSep 91419 resin, where Au-cyanide was eluted using a potassium thiocyanate solution with a flow rate of 10 BV/h. In this case, it only took 2 hours to elute 83% of the Au (Schoeman et al., 2013). This rapid elution can be attributed to the resin's high affinity towards thiocyanate, as well as the high flow rate, which may not be feasible in a full-scale process.

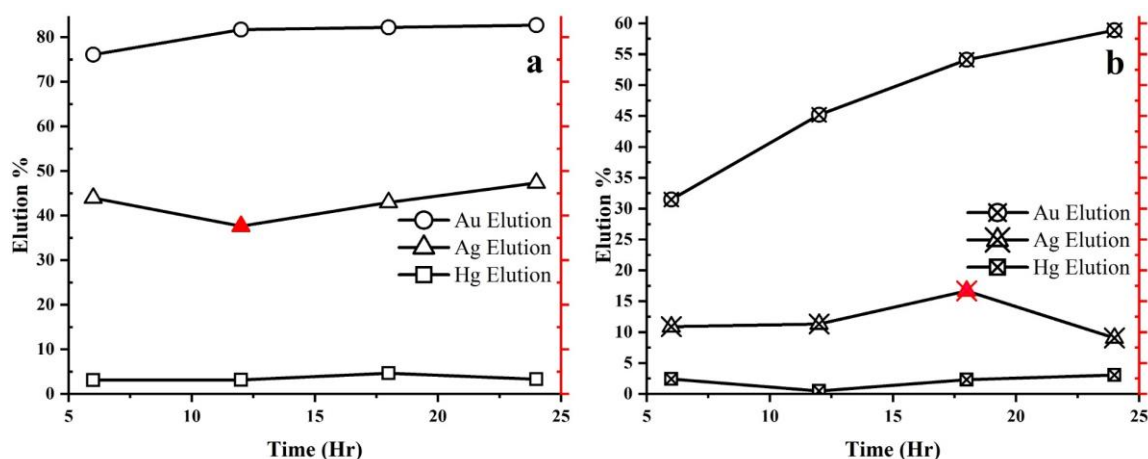


Figure 40. Effect of retention time on elution of Purolite 500Cplus (a) and AmberSep 91419 (b), at NaCl 150 g/l, NaOH 5 g/l, NaClO 0.75%, BV 40, temperature 40 °C and shaking speed 200 rpm.

The impact of retention time on the elution of Au and Ag from Purolite 500Cplus and AmberSep 91419 resins was investigated. Based on the findings of previous studies and preliminary tests, The elution time range was determined to be between 6 and 24 hours, with 6-hour intervals. The results are depicted in Figure 40. Surprisingly, the increase in elution time did not exhibit a significant influence on the elution of Au and Ag from Purolite 500Cplus resin. Extending the elution time from 6 to 12 hours only resulted in a marginal improvement of 5% in Au elution, from 76% to 81.7%, while simultaneously causing a decline in Ag elution from 43% to 37.6%. Moreover, prolonging the retention time beyond 12 hours did not yield any further enhancement in Au elution, although it did lead to a slight increase that of Ag to 47%. In contrast, the effect of retention time on the elution of Au from AmberSep 91419 resin was more pronounced, particularly within the first 12 hours. Increasing the time from 6 to 18 hours resulted in a substantial improvement in Au elution, to increase from 31.5% to 54%. However, the elution of Ag remained relatively unchanged within the same time frame. Interestingly, extending the elution time to 24 hours further enhanced Au elution to approximately 59%, but it caused a decrease in Ag elution from 16%

to 9%. It is noteworthy that the improvement in the elution of Au from Purolite 500Cplus resin ceased after the 12th hour, while the that of Au from AmberSep 91419 resin became more pronounced over time. To ascertain the most suitable duration for the elution process using these resins, it is advisable to conduct kinetic elution tests putting into consideration the electrowinning process.

4.6.5. Effect of Temperature

Fleming and Cromberge (1984) conducted a study to investigate the impact of temperature on the elution of aurocyanide by zinc cyanide and thiosulfate from strong base IX resin. They found that both the efficiency of elution and the rate of electrolytic deposition were enhanced as the temperature increased. Specifically, when the temperature was increased from 20°C to 60°C, the elution increased from 66% to 98% using a 0.15M concentration of Zn(CN)_4^{2-} . However, it was observed that by using a 2M concentration of NH_4SCN solution, complete elution of gold could be achieved at room temperature. In contrast, Staker and Sandberg (1987) reported achieving less than 95% elution by utilizing a mixture of NaCl, NaOH, and NaClO at ambient temperature. The results obtained from these studies highlight the importance of temperature as a key determinant that should be carefully evaluated in relation to gold elution.

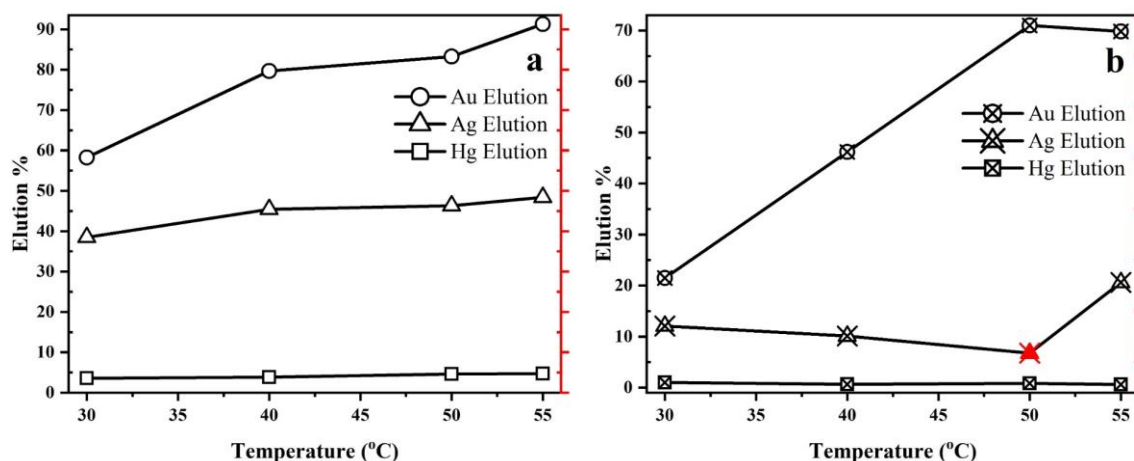


Figure 41. Effect of temperature on elution of Purolite 500Cplus (a) and AmberSep 91419 (b), at NaCl 150 g/l, NaOH 5 g/l, NaClO 0.75%, BV 40, retention time 12 hours and shaking speed 200 rpm.

The impact of temperature on the elution of Au-glycinate complex was examined. The results in Figure 41 indicated that the elution of Au from both Purolite 500Cplus and AmberSep 91419 resins was positively influenced by increasing the temperature. Specifically, for Purolite 500Cplus, raising the temperature from 30 to 40 °C resulted in an enhancement of Au elution from 58% to 79%. Further increase in temperature to 50 °C led to a slight increase in elution by approximately 3.5%. In the case of AmberSep 91419, the desorption of Au exhibited a linearly sharp increase with temperature elevation within the range of 30-50 °C. Elevating the temperature to 55 °C achieved 91% gold elution from Purolite 500Cplus resin, while it did not affect its elution from AmberSep 91419. Regarding Ag elution, the effect of temperature on its elution from Purolite 500Cplus was generally slightly positive, whereas it had a negative impact on Ag elution from AmberSep 91419 up to 50 °C, before unexpectedly becoming positive at 55 °C. These findings align with a previous study conducted by Schoeman, et al. (2017), which reported the elution of 70% Au from Amberlite PWA5 strong base IX loaded with Au-cyanide using a 2M KSCN solution at 50 °C, and 53% of Au using solution of $0.5 \text{ Zn(CN)}_4^{2-}$ at 60 °C.

The resins employed in this study can efficiently work in a temperature range up to 60 °C when they are in Cl⁻ form. To avoid any potential degradation, the upper temperature limit for this investigation was adjusted to 55 °C. Nevertheless, upon reaching 55 °C, the resin exhibited a noticeable pale-yellow hue, which could indicate impending deterioration. Therefore, it is advisable not to use temperature more than 50 °C, to ensure optimal performance and longevity of the resin.

4.6.6. Gold Elution Kinetics

After establishing the optimal conditions for the Au elution process, which include NaCl concentration of 150 g/l, NaOH concentration of 5 g/l, NaClO concentration of 1% v/v, bed volume (BV) of 80, retention time of 12 hours, temperature of 50 °C, and shaking speed of 200 rpm, the elution of Au over time was examined for both Purolite and AmberSep resins using these predetermined conditions. The findings presented in Figure 42 demonstrate that the elution of Purolite resin is significantly more efficient compared to AmberSep resin. Within the first hour, more than 80% of the Au was successfully eluted from Purolite A500, whereas it took over 6 hours to achieve the same level of elution from AmberSep resin. Notably, the elution process for Purolite resin could be completed within

12 hours, resulting in the desorption of 98% of the Au. Conversely, it took 18 hours for AmberSep resin to be completely eluted. These observations were made during the patch elution tests. However, in continuous elution-electrowinning processes, the time limitation of the process is determined by the rate at which the Au is reduced at the Cathode, rather than the duration required for elution.

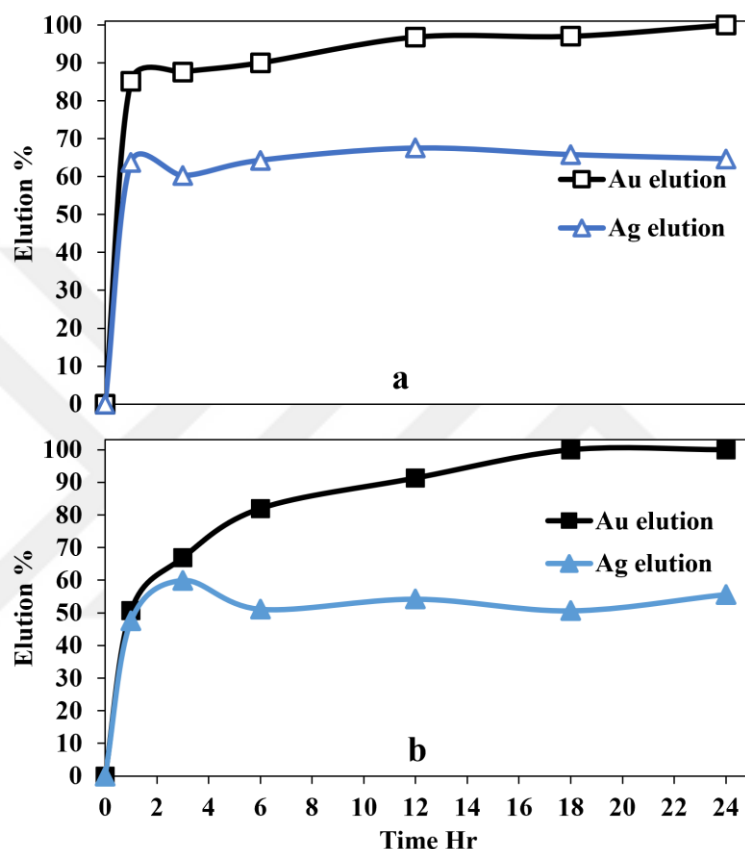


Figure 42. Kinetics of Au and Ag elution from Purolite 500Cplus (a) and AmberSep 91419 (b). NaCl 150 g/l, NaOH 5 g/l, NaClO 1% v/v, (BV) 80, retention time of 12 hours, temperature 50 °C, and shaking speed of 200 rpm.

4.6.7. Cycle Test

Oraby and Deng (2020) conducted a study to examine the reusability of IXOS resin through a series of adsorption/elution cycles. They utilized alkaline sodium thiocyanate (2.5 M) and acidic thiourea (0.5 M thiourea/0.5 M H₂SO₄) for gold elution, and a 0.4 M NaCN solution for copper elution. The resin was subjected to agitation with 40BV at a temperature

of 55 °C for a duration of 6 hours. The evaluation of the resin was based on changes in loading capacity and regeneration efficiency (RE%).

Table 22. Results of Au, Ag and Hg multicycle Adsorption/Desorption conducted on Purolite resin.

Adsorption cycle	Au adsorption capacity mg/g	RE %	Ag adsorption capacity mg/g	RE %	Hg adsorption capacity mg/g	RE %
1	3.303	100	0.932	100	2.93	100
2	3.234	97	1.109	84	2.17	74
3	3.338	96	0.773	79	1.96	67
4	3.208	96	0.841	74	1.95	67
5	3.213	94	0.819	71	1.49	51
Hg Elution	Au E%	Residual Au mg/g	Ag E%	Residual Ag mg/g	Hg E%	Residual Hg mg/g
1	1.63	3.249	0.61	0.926	96.77	0.095
2	2.07	3.168	1.04	1.097	87.28	0.288
3	2.27	3.263	4.98	0.735	79.29	0.446
4	2.22	3.137	8.01	0.773	47.07	1.167
5	2.49	3.133	6.64	0.765	51.87	1.159
Au Elution	Au E%	Residual Au mg/g	Ag E%	Residual Ag mg/g	Hg E%	Residual Hg mg/g
1	99.39	0	65.70	0.314	6.76	0
2	94.24	0.120	67.53	0.349	12.22	0.011
3	93.46	0.143	75.74	0.149	9.47	0.242
4	94.75	0.097	63.96	0.236	29.32	0.521
5	92.12	0.173	73.24	0.165	41.70	0.155

The findings of the study indicated that the efficiency of gold and copper elution (E%) remained consistently high at approximately 97% - 98% for thiourea elution system. Moreover, the gold adsorption capacity exhibited a slight increase, while the copper adsorption capacity decreased after three cycles of adsorption/elution. When sodium thiocyanate and cyanide processes were employed, the efficiency of gold and copper elution (E%) decreased to 92% and 93% respectively. However, the gold adsorption capacity increased after the first cycle and remained constant during the second and third adsorption cycles. On the other hand, the copper adsorption capacity decreased after the three adsorption cycles.

The current study involved conducting multiple adsorption/elution cycle tests, which were repeated five times. H_2SO_4 was used to elute Hg, while a mixture of NaOCl, NaCl, and NaOH was used to elute Au and Ag. The elution of Hg was carried out under specific conditions, including an eluent concentration of 0.5 M, a solution BV of 40, an elution time of 4 hours, an environmental temperature of 25 °C, and a shaking speed of 200 rpm. On the other hand, the multiple tests for Au and Ag were conducted under different conditions, included a NaCl concentration of 150 g/l, NaOCl concentration of 1% v/v, NaOH concentration of 5 g/l, eluent volume of 80 BV, elution time of 24 hours (considering the electrowinning process), elution temperature of 50 °C, and shaking speed of 200 rpm.

The results presented in Table 22 indicate that the loading capacity of the Purolite A500Cplus resin for Au did not significantly decrease, and the regeneration efficiency remained relatively stable. However, the loading capacity and regeneration efficiency of Ag and Hg deteriorated significantly, reaching only 71% and 51% of the initial regeneration efficiency, respectively. During the elution process of mercury, unexceptionally the three metals exhibited an undesirable elution profile. While the elution of Au and Ag slightly increased to reach 2.5% and 6.64%, respectively, in the fifth cycle, the elution of Hg gradually declined from 96% to 51%. In the elution stage of Au and Ag, the elution of Au showed a good profile throughout all cycles, while the elution of Ag remained between 65% and 73%. It is worth noting that the elution of Hg increased alongside Au and Ag, which could pose challenges in downstream processes. However, this observation opens avenues for further research on bulk elution of Au, Ag, and Hg using the same eluent.

Table 23 illustrates the results of the adsorption/ elution multi-cycle test conducted on AmberSep 91419 resin for the removal of Hg, Au, and Ag. It is evident that the adsorption capacity and RE% of Au experienced a slight decrease over the course of five cycles,

reaching 87%. On the other hand, Ag RE% exhibited a significant decline, dropping to approximately 33%, while Hg decreased to around 58%.

Table 23. Results of Au, Ag and Hg multicycle Adsorption/Desorption conducted on AmberSep 91419 resin.

Adsorption cycle	Au adsorption capacity mg/g	RE %	Ag adsorption capacity mg/g	RE %	Hg adsorption capacity mg/g	RE %
1	3.366	100	0.965	100	2.97	100
2	3.310	96	1.144	71	2.13	72
3	3.211	92	0.601	55	2.07	70
4	3.201	91	0.751	50	1.88	63
5	3.043	87	0.435	33	1.73	58
Hg elution	Au E%	Residual Au mg/g	Ag E%	Residual Ag mg/g	Hg E%	Residual Hg mg/g
1	1.00	3.332	4.92	0.918	94.38	0.167
2	1.16	3.272	6.35	1.072	85.12	0.342
3	1.19	3.173	12.87	0.524	82.51	0.392
4	1.17	3.164	10.57	0.672	44.12	1.173
5	1.28	3.004	24.42	0.359	50.18	1.337
Au elution	Au E%	Residual Au mg/g	Ag E%	Residual Ag mg/g	Hg E%	Residual Hg mg/g
1	97.69	0.044	52.70	0.409	5.70	-0.02
2	94.55	0.142	54.10	0.453	12.05	0.065
3	92.44	0.205	44.31	0.257	12.49	0.112
4	92.47	0.204	49.20	0.302	50.79	0.107
5	92.53	0.188	42.48	0.157	42.72	0.190

During the Hg elution stage, the elution efficiency decreased from 94% in the first cycle to 50% at the end of the test. In contrast, the elution of Au remained constant at 1%, whereas Ag elution increased substantially from approximately 5% at the beginning of the test to 24% at the end, indicating a significant loss of Ag in the mercury elution stream.

Regarding the Au elution stage, the desorption of gold decreased from 98% in the first cycle to 94.5% in the second cycle, and then stabilized at 92% for the remaining cycles. The elution efficiency of Ag remained consistent between 54% and 42% throughout all the cycles. However, Hg elution increased from 5% in the initial stage to 12% and 51% in the first, second, and fourth cycles, respectively, before declining to 42% in the final cycle. The presence of this amount of Hg in the Au elution stream could potentially lead to various complications during the electrowinning, cementation, or smelting stages.

4.6.8. Adsorbents Characterization

The good Au adsorption capacity of both resins can be attributed to their strong affinity for Au and the efficient elution of Au, which mentioned above 94% up to the last cycle. This allows the Au-glycinate complex to be adsorbed onto the resins in subsequent cycles. However, the poor regeneration efficiency of Ag can be attributed to its inadequate elution from the resins, resulting in the deposition of Ag on the resin surface, reaching levels higher than 0.450 mg/g in certain cycles. The decline in Hg elution can be attributed to two factors. Firstly, the osmotic shock experienced during the acidic and basic elution stages may contribute to this deterioration. Secondly, the high concentration of sodium chloride (NaCl) used may cause blockage of the macropores in the Purolite resin, as shown in Figure 43, where the surface morphology of the resin gradually disappears after the cycle tests, unlike the fresh resin and resin eluted only once, which maintain a clear surface morphology. Similarly, the deposition of a significant amount of NaCl on the surface of the AmberSep resin, as depicted in Figure 44, hinders the elution of adsorbed metals and makes it challenging to adsorb additional metals onto the resin.

The findings from the multicycle tests revealed that the Au adsorption capacity of both resins remained unaffected. However, there was a significant decline in the adsorption capacity of Ag and Ag, and the reasons for this decline were explained. To support the hypothesis of NaCl deposition on the resin surface and to identify the presence of metals on the resins during the cycle tests, SEM-EDS profiles were generated for both resins.

Figure 45 displays the EDS profile of Purolite A500Cplus after undergoing 5 cycles. The profile indicates that the resin contains high levels of chlorine coming from the eluent, along with some traces of mercury and silver. However, the presence of mercury and silver cannot be fully trusted due to the high standard deviation. Nevertheless, this finding aligns with the results presented in Table 23, which confirmed the presence of Hg and Ag on the resin surface at the end of the tests. Interestingly, no Au was detected.

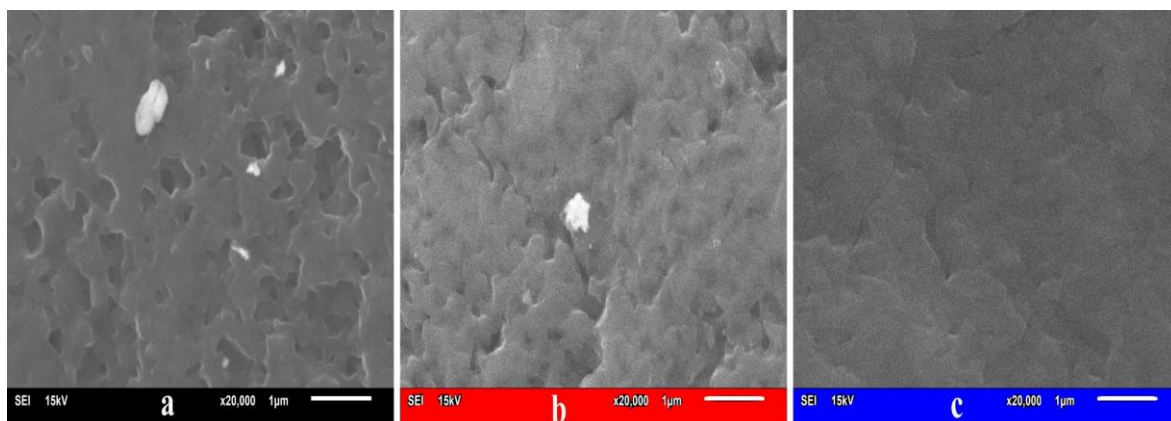


Figure 43. Purolite A500Cplus resin, SEM pictures for at low magnification for fresh resin (a), one-time eluted resin (b) five time loaded/eluted resin (c)

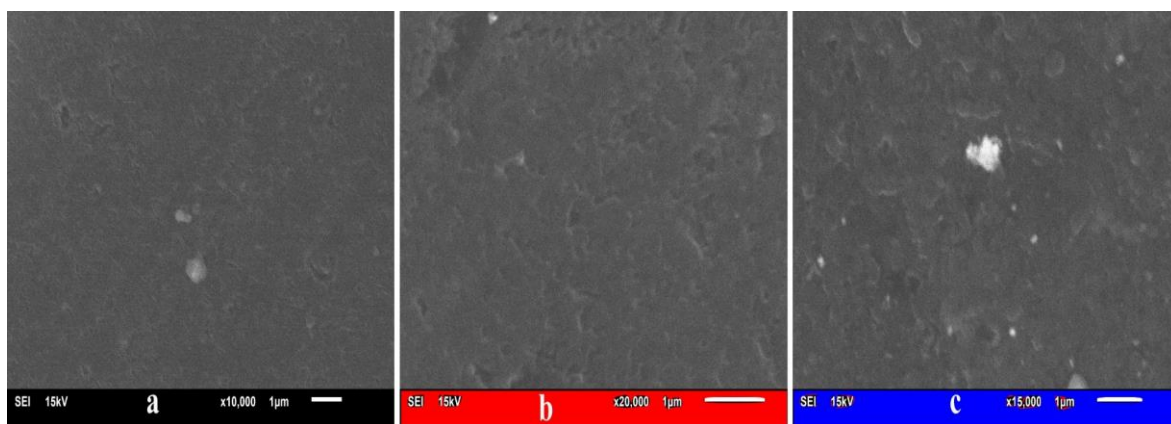


Figure 44. AmberSep 91419 resin, SEM pictures for at low magnification for fresh resin (a), one-time eluted resin (b) five time loaded/eluted resin (c).

On the other hand, Figure 46 illustrates the EDS spectra of AmberSep 91419, which also shows the presence of chlorine. However, no metals were detected. This could be attributed to the possibility of these metals being located in the deeper layers of the resin pores rather than on the resin surface.

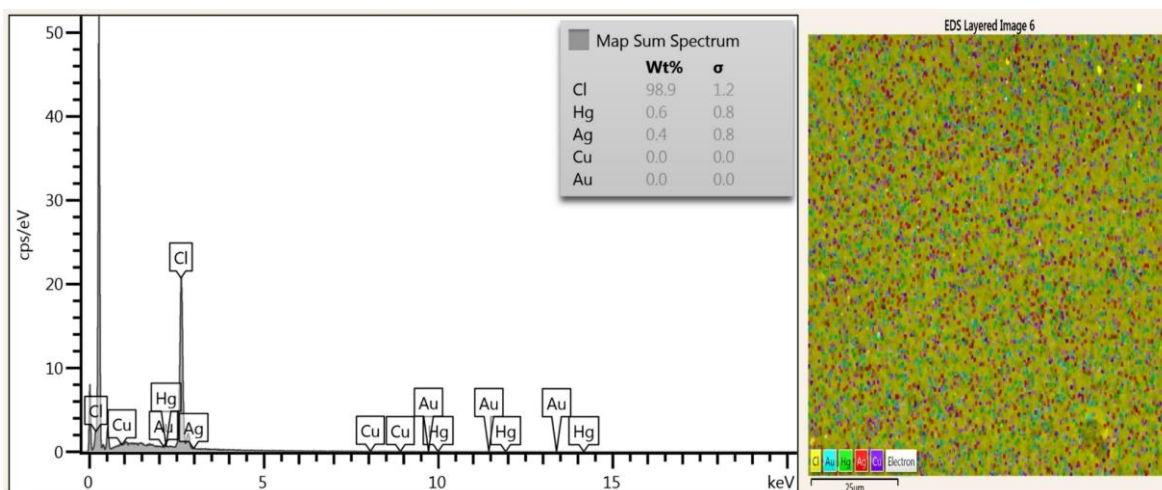


Figure 45. SEM-EDS profile of Purolite A500Cplus after 5 cycles of adsorption/ elution

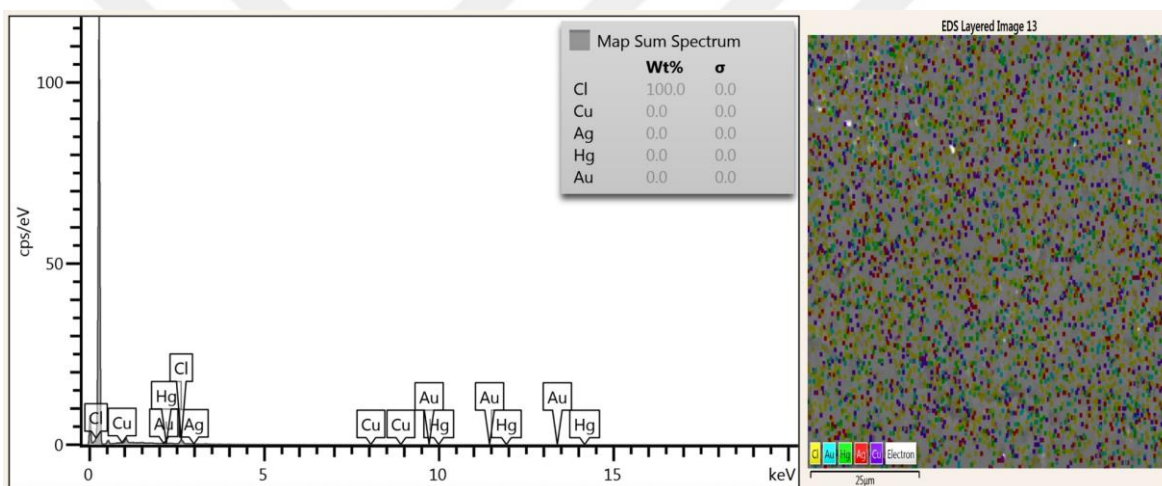


Figure 46. SEM-EDS profile of AmberSep 91419 after 5 cycles of adsorption/ elution

To evaluate the physical state of the resin and investigate the presence of significant deterioration such as breakage, cracks, and rifts after adsorption and multiple adsorption/elution tests, low magnification scanning electron microscopy (SEM) images were obtained for the raw resin, loaded resin, resin after one-time elution, and resin subjected to multicycle tests. As depicted in Figures 47 and 48, the fresh resins appeared as smooth spherical polymer particles without any visible indication of a porous structure at this level of magnification. It was also observed that the resins did not experience any degradation.

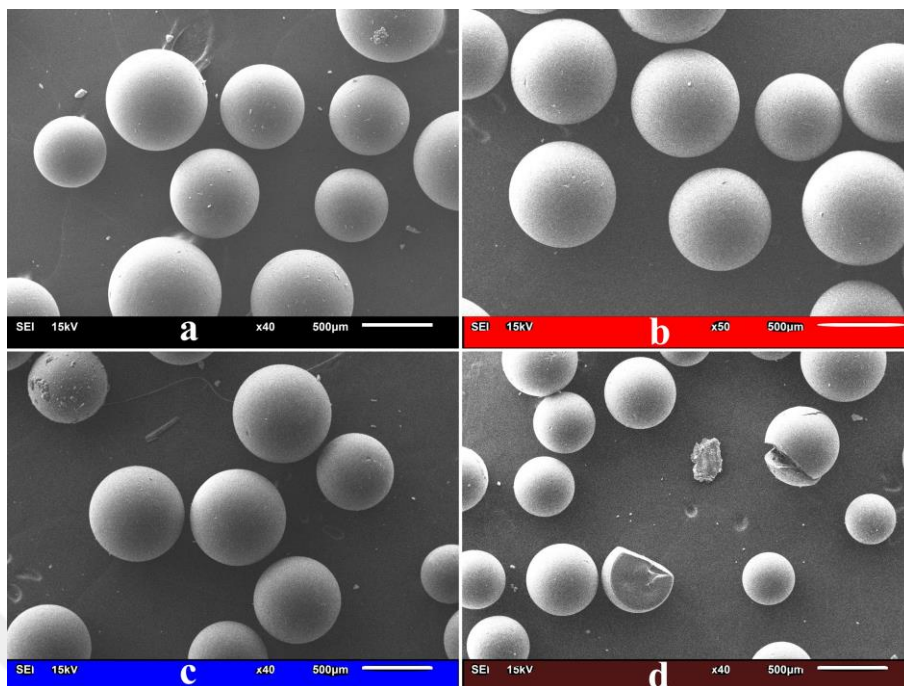


Figure 47. Purolite A500Cplus resin, low magnification SEM pictures for fresh resin (a), Loaded resins (b) one-time eluted resin (c) five time loaded/eluted resin (d).

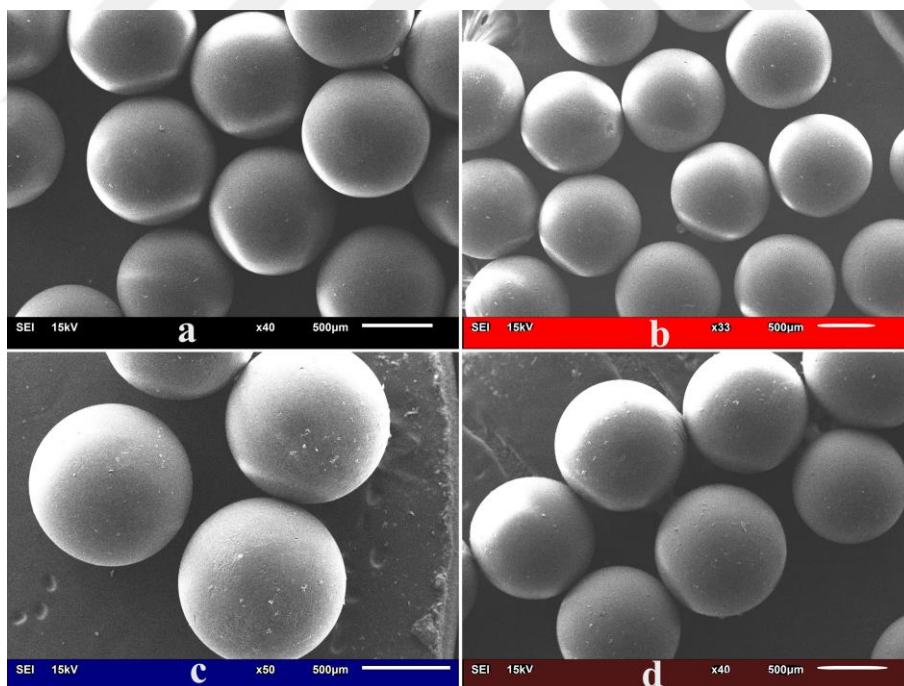


Figure 48. AmberSep 91419 resin, low magnification SEM pictures for fresh resin (a), Loaded resins (b) one-time eluted resin (c) five time loaded/eluted resin (d).

during the adsorption and one-time elution stages. However, during the multicycle adsorption/desorption tests, the Purolite A500Cplus resin exhibited significant degradation,

while the AmberSep 91419 resin remained physically unaffected. The degradation of the Purolite resin is likely attributed to the osmotic shock generated by repeated elution in an acidic environment and adsorption in alkaline conditions (Deng, et al., 2020). Similar findings were reported by Deng, et al. (2020) in their investigation of copper elution from ion exchange resin using a mixture of glycine, NaCl, and NaOH. They also attributed the resin degradation to the agitation during the adsorption/desorption process and the attrition between the resins.

The FTIR data of Purolite A500 was interpreted according to researchers have been done on a similar kind of resins. As it is presented in Figure 49, The presence of -OH and -NH stretching vibrations was indicated by the boarder band at 3365, 3390, and 3358 cm^{-1} . The -CH stretching vibration in -CH and -CH_2 was indicated by the band at 2929, 2930, and 2919 cm^{-1} in the fresh, loaded, and eluted resins (Costache et al., 2008). The aromatic skeleton ($\text{C}=\text{C}$ bonds) from poly(styrene-co-divinylbenzene), which is the matrix of A500 resin, was represented by the band at 1635, 1475, and 1240 cm^{-1} (Fu et al., 2020). The presence of -CO corresponding to C-N in -COH was indicated by the band at 974 cm^{-1} (Costache et al., 2015). The bands at 889 cm^{-1} , 855 cm^{-1} , and 830 cm^{-1} in the fresh resin corresponded to stretching vibration of C-Cl in vinyl benzyl chloride monomer, which shifted to 829 cm^{-1} after the adsorption of metals and to 824 cm^{-1} after the elution (Azizitorghabeh et al., 2023). The low transmittance at the eluted resin indicated a substantial reduction in metal content.

As it is the case for the former IX resin, the FT-IR spectra of AmberSep 91419 exhibited distinct peaks as it is presented in Figure 50. A transmission band at 3365 cm^{-1} was observed, which was attributed to the presence of -NH and -OH groups. Additionally, a peak at 2926 cm^{-1} indicated the stretching vibration of -CH bonds (Hafsa et al., 2019). The significant size of the peak at 3365 cm^{-1} in the fresh resin could be attributed to its high moisture content. Moreover, peaks at 1601 cm^{-1} were assigned to O-H bending. The two characteristic peaks at 1493 cm^{-1} and 1377 cm^{-1} were identified as C-H bending and C-N stretching vibrations of the quaternary ammonium functional group in the anion resin (Tandorn et al., 2019). Notably, the shift of the peak from 1377 cm^{-1} in the fresh resin to 1330 cm^{-1} in the loaded resin indicated the adsorption of metal ions onto the resin. Overall, the resin maintained its characteristics after the elution process, except for the peak at 1025 cm^{-1} , which shifted to 960 cm^{-1} post-elution.

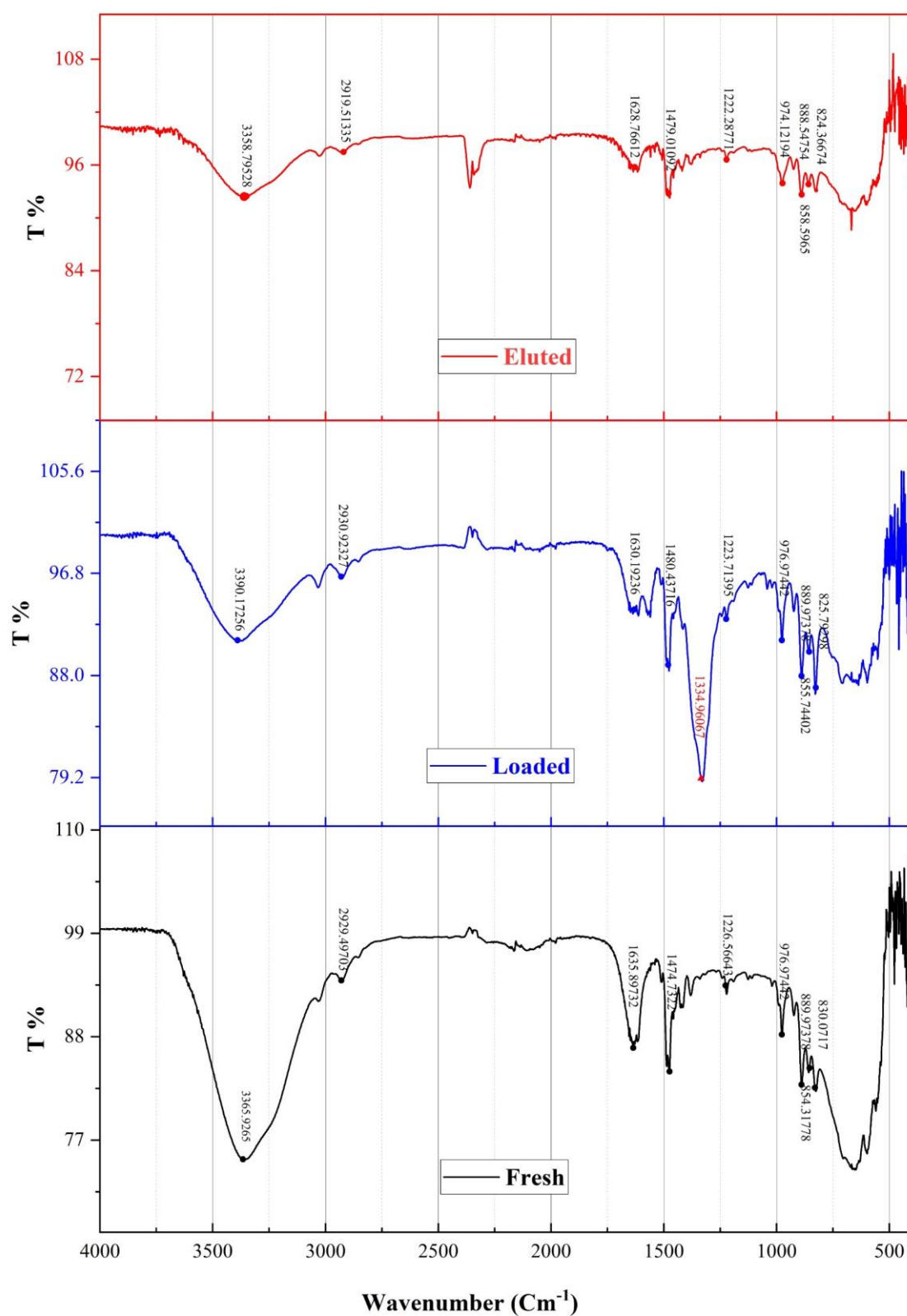


Figure 49. FTIR spectra of fresh, loaded, and eluted Purolite A500Cplus resin.

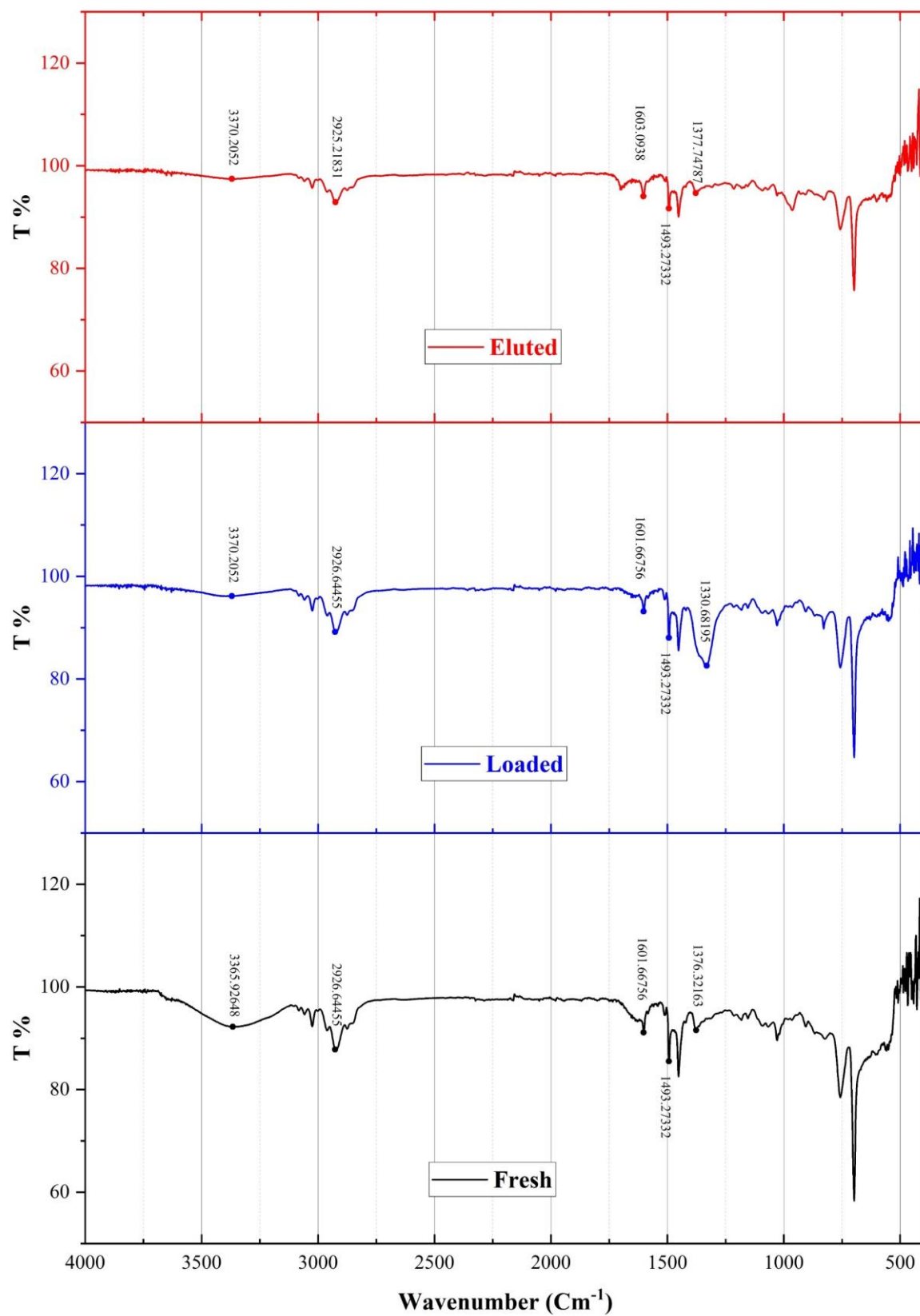


Figure 50. FTIR spectra of fresh, loaded, and eluted AmberSep 91419 resin.

5. CONCLUSION

The experimental work was conducted to achieve the main objective of the thesis, which is the selective recovery of Au and Hg from Glycine pregnant solution. The initial step involved characterizing the samples, which revealed that the sample primarily consisted of Quartz, along with various iron and titanium minerals such as Rutile. The grades of Au, Ag, Cu, and Hg in the sample were found to be 14.45, 4.07, 275, and 8 ppm, respectively.

To selectively recover the metals, three different adsorbents were chosen: Purolite A500 CPlus, AmberSep M91419, and MFCARB GC E612 activated carbon. The optimal conditions for the process were determined to be 30 °C for temperature, 10.5 for pH, 2 g/l for adsorbent dosage, 12 hours for retention time, and 150 rpm for shaking speed. Under these conditions, the adsorption of metals onto all adsorbents approached 100%, except for Hg loading onto AC, which reached only 80%. The results of the adsorption kinetics and isotherms indicated that the PSO kinetics model governed the adsorption behaviour of Au and Hg onto all adsorbents. Furthermore, the adsorption isotherm of Au onto IX resin showed a better fit with the Freundlich model, while its adsorption isotherm onto AC aligned with the Langmuir model.

After successfully optimizing the adsorption process, the elution of Hg and Au was carried out. The optimal conditions for maximum Hg elution were determined to be an eluent concentration of 0.5 M H₂SO₄, a solution bed volume of 40, an elution time of 4 hours, and an environmental temperature of 25 °C. Under these conditions, 100% of Hg and approximately 1% of Au were successfully eluted from both resins.

For the elution of Au, the optimal conditions were found to be a NaCl concentration of 150 g/l, NaOCl concentration of 1% v/v, NaOH concentration of 5 g/l, eluent volume of 80 bed volumes, elution time of 24 hours (considering the electrowinning process), and elution temperature of 50 °C. Under these conditions, 100% of Au was effectively eluted from both resins, while 65% and 55% of Ag were eluted from Purolite 500Cplus and AmberSep 91419. However, during the pretest of the elution process, it was observed that AC carbon was difficult to elute during both Hg and Au elution stages, leading to its exclusion from further research.

Cycle tests revealed that the gold elution efficiency (E%) and regeneration efficiency (RE%) remained relatively high for both resins, while the values for silver and mercury

significantly decreased over five cycles. SEM images showed that the Purolite resin underwent physical degradation, making it unsuitable for further use. On the other hand, the AmberSep resin exhibited promising characteristics, indicating its suitability for future research endeavours and industrialization projects.

The present study has furnished an innovative, thorough, and satisfactory body of knowledge regarding the adsorption and selective desorption of gold and silver from glycine pregnant solution using IX resins and Activated carbon. which hold great potential in facilitating the application of the recently developed glycine leaching process. Nevertheless, certain positive observations, concerns, and challenges were encountered during the elution stage, particularly in relation to silver, for which a range of advancements and solutions have been proposed.



6. PROPOSED FURTHER WORK

Throughout this thesis, the focus was on studying the adsorption of metals onto activated carbon and IX resins, as well as analysing the kinetics and isotherm model fitting. Additionally, the selective elution of Au and Hg was carried out, along with investigating the elution kinetics and cycle tests. The optimization of the adsorption process yielded satisfactory results. However, there are several aspects related to the elution process that require further investigation.

In general, the selective elution process of Au and Hg from both resins was successful. However, the elution of Ag was relatively low. To address this issue, it is proposed to explore the addition of hydrochloric acid to the elution mixture in order to enhance the desorption of Ag. It is important to note that the pH should be maintained above 7 to prevent any degradation of the resin. Furthermore, during the course of this research, it was observed that a mixture of NaClO, NaOH, NaCl has the potential to effectively elute Hg from the IX resin. This finding presents an interesting avenue for further investigation into the bulk elution of Au, Ag, and Hg, while incorporating the aforementioned suggestion of adding HCl. Moreover, it is recommended to comprehensively study the selective cementation of mercury and Au, Ag from the bulk elution solution.

Moreover, the use of batch elution tests revealed that a significant amount of solution is required to achieve complete elution of Au. This raises the question of whether it is possible to reduce the volume of the eluent by conducting desorption tests in a continuous system. To explore this possibility, the researchers propose the implementation of a continuous elution electrowinning system, in addition to conducting a comprehensive investigation of the electrowinning process.

Lastly, during the multicycle tests, it was observed that the high concentration of NaCl had a negative impact on the adsorption capacity of the resins, particularly for Ag and Hg. Therefore, it may be worthwhile to conduct further research using a smaller amount of NaCl, along with NaClO, NaOH, and HCl.

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BIOGRAPHY

Abdulbagi Hassan Abdallah MOHAMED, embarked on his educational journey in 2001 at Al-qa'a Primary School. He successfully completed his primary education in 2009 and then proceeded to Para, where he pursued his secondary education at Para Al-Janobia Secondary School for two years. In 2012, he relocated to Omdurman and completed the third year of secondary school at AL-Farouq Secondary School for Boys, ultimately graduating in the same year.

Following his secondary education, Mr. Abdulbagi joined Omdurman Islamic University in 2012. He excelled in his studies and was awarded a first-class B.Sc. degree with honours in mining engineering, specializing in the Minerals Processing division, in 2017. During his undergraduate studies, he focused on the enrichment of Chromite ore through the utilization of heavy media separation techniques. Upon the completion of his bachelor's degree, Mr. Abdulbagi was appointed as a part-time teaching assistant at the Department of Mining Engineering in his alma mater, starting in September 2017. In December 2018, he embarked on a new professional endeavour as a mining engineer and Occupational Health and Safety (OHS) engineer at BN For Mining. Subsequently, in September 2019, he assumed the role of an English and Science teacher at AlQuerawn Quranic English Academy.

In recognition of his academic achievements, Mr. Abdulbagi was granted a postgraduate scholarship by the Turkish government in 2020 to pursue his master's studies in Türkiye. He commenced his MSc in Mining Engineering at the Division of Mineral Processing, Mining Engineering Department of Karadeniz Technical University. Prior to starting his master's program in October 2021, he completed a one-year Turkish language preparatory program. During his master's studies, which spanned from October 2021 to February 2024, Mr. Abdulbagi concurrently worked for ERGOLD Innovation company in the R&D unit, focusing on mineral processing and hydrometallurgical projects. He actively participated in various competitive research and technology development platforms such as specifically aiming to develop a new environmentally friendly technology to replace the use of Cyanidation process in mercury-containing primary and secondary resources. Notably, Mr. Abdulbagi possesses fluency in Arabic, English, and Turkish.