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Adsorption of Arsenic on Lanthanum and Cerium nanoparticles adsorbents during hydrometallurgical extraction of Copper

by

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(218045808)

A Master’s Research dissertation submitted in fulfilment of the requirements for the degree of

[POSTGRADUATE DEGREE – Master of Technology]

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[EXTRACTION METALLURGY]

in the

Faculty of Engineering and the Built Environment

at the

UNIVERSITY OF JOHANNESBURG

SUPERVISOR: PROF. MAMOOKHO ELIZABETH MAKHATHA
CO SUPERVISOR: PROF. WILLIE. NHETA

[5th August 2019]
DEDICATION

To mum, dad and my siblings. Also, to everyone who made my time in Johannesburg interesting.
DECLARATION

I Emmanuel Anuoluwa Bamidele write to declare that this master’s research dissertation is my own work in its entirety. I have not submitted it anywhere else for academic credit by myself or another person. I understand the meaning of plagiarism and I hereby declare the ownership of the phrase, words, ideas, figures, graphics, results and organization except where reference is explicitly made to another’s work. I understand further that any unethical academic behavior, which includes plagiarism, is seen in a serious light by the University of Johannesburg and is punishable by disciplinary action.

Signed ……………………… Date: 27 October 2019
ACKNOWLEDGEMENT

First, all glory and adoration belong to God almighty for giving me good health and blessing me with sound mind to carry out this project.

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ABSTRACT

Various activities of mining, mineral processing and extraction releases arsenic into the environment. The reported presence of high concentration of arsenic in lakes surrounding a selected silver, cobalt and copper mines has gained serious attention of the scientific community. This research encompasses the characterization of a low-grade copper oxide ore using atomic absorption spectrometer, x-ray fluorescence (XRF), x-ray diffractometer (XRD), SEM-EDS and Induced Coupled Plasma Mass Spectroscopy (ICP-MS). Leaching and adsorption of the copper ore sample was carried out using sulphuric acid of varying molarity -3M, 2M, 1.5M, 1M and 0.5M – and two Lanthanum and Cerium nanoparticles adsorbents were prepared for the adsorption of arsenic from the ore sample during the hydrometallurgical extraction of copper leaching process. This study revealed that there is a direct relationship between the concentration of acid and arsenic dissolution. The %As adsorption on Lanthanum nanoparticles adsorbent is lower at higher acid molarity and higher at lower sulphuric acid molarity. While in the case of Cerium adsorbent, there is a deviation. The Cerium ions were able to actively react with arsenic at higher acid molarity hence causing higher adsorption at higher molarity of acid than lower molar mass. Arsenate removal efficiency increases sharply with increasing adsorbent dosage, though there were some anomalies which were observed to be because of competing ions on the adsorption. The increase in temperature was found to reduce the adsorption efficiency of both the Cerium and Lanthanum nanoparticles adsorbents. The effect of acid molarity, adsorbent dosage and temperature were also studied on copper and iron dissolution in the extraction process. Low copper dissolution rate was achieved due to the activation of active binding sites by the Cerium and Lanthanum adsorbents which might have attracted some copper ions. The copper dissolution rate obtained when Cerium impregnated adsorbent was used gave better copper recovery than when Lanthanum adsorbents were applied. The values of \( R_L \) obtained for each of the adsorption carried out shows that the nature of Langmuir model is unfavourable for Lanthanum nanoparticles, but the linear value obtained for \( R_L \) in the case of Cerium nanoparticles makes it fit into the model. It is important to note that Cerium nanoparticles adsorbent performs better with increasing acid molarity while Lanthanum nanoparticles adsorbent performs better with increasing adsorbent dosage. Considering the findings obtained from studying different parameters such as acid molarity, temperature and adsorbent dosage, it can be concluded that Cerium nano adsorbent is a better adsorbent than Lanthanum nano adsorbent.
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**LIST OF ABBREVIATIONS**

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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AAS</td>
<td>Atomic Adsorption Spectroscopy</td>
</tr>
<tr>
<td>AD</td>
<td>Anno Domini</td>
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<tr>
<td>ALS</td>
<td>Amyotrophic Lateral Sclerosis</td>
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<tr>
<td>BC</td>
<td>Before Christ</td>
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<tr>
<td>BMI</td>
<td>Business Monitor International</td>
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<tr>
<td>CED</td>
<td>Chronic Energy Deficiency</td>
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<tr>
<td>CeFP</td>
<td>Cerium Fibrous Protein</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic Acid</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
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<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
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<tr>
<td>PED</td>
<td>Protein Energy Deficiency</td>
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<tr>
<td>PLS</td>
<td>Pregnant Leach Solution</td>
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<td>PM</td>
<td>Particulate Matter</td>
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<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>WHO</td>
<td>World Health Organization</td>
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<tr>
<td>XRF</td>
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<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS

DEDICATION ........................................................................................................................................ ii
DECLARATION ..................................................................................................................................... iii
ACKNOWLEDGEMENT ........................................................................................................................ iv
ABSTRACT .......................................................................................................................................... v
LIST OF PUBLICATIONS ..................................................................................................................... vi
LIST OF ABBREVIATIONS ................................................................................................................... vii
TABLE OF CONTENTS ........................................................................................................................ viii
LIST OF TABLES .................................................................................................................................. xi
LIST OF FIGURES ............................................................................................................................... xii

1. CHAPTER 1: INTRODUCTION ........................................................................................................... 13
   1.1. BACKGROUND .......................................................................................................................... 13
   1.2. RESEARCH PROBLEM STATEMENT ..................................................................................... 15
   1.3. RESEARCH QUESTIONS ......................................................................................................... 16
   1.4. RESEARCH OBJECTIVES OF THE STUDY .......................................................................... 17
   1.5. RESEARCH MOTIVATION ..................................................................................................... 17
   1.6. SIGNIFICANCE OF THE STUDY .......................................................................................... 17
   1.7. RESEARCH METHODOLOGY ............................................................................................... 18
   1.8. DELIMITATION ..................................................................................................................... 18
   1.9. STRUCTURE OF DISSERTATION .......................................................................................... 18

2. CHAPTER 2: LITERATURE REVIEW ............................................................................................... 20
   2.1. OCCURRENCE OF COPPER MINERALS .............................................................................. 20
       2.1.1. Petrology and Microscopy of Copper Minerals .............................................................. 20
       2.1.2. Characterization ............................................................................................................. 20
   2.2. PROCESSING OF COPPER ORE ............................................................................................. 21
   2.3. LEACHING OF COPPER ORE ............................................................................................... 22
   2.4. ARSENIC, ENVIRONMENTAL IMPACTS AND ADSORPTION ............................................. 23
       2.4.1. Chemistry of Arsenic ....................................................................................................... 23
       2.4.2. Ecological Impacts of Arsenic ....................................................................................... 23
       2.4.3. Environmental Effects of Arsenic and Other Trace Impurities .................................... 24
       2.4.4. Effects of Arsenic Contamination on Human Health ................................................ 25
       2.4.5. Effect of Arsenic Contamination on Animals .............................................................. 28
2.4.6. Immobilization of Arsenic in Aqueous Solution: Application in Hydrometallurgical Extraction of Copper .......................................................... 30
2.4.7. Adsorption of Arsenic from Copper Oxide leaching solution ................................. 32
2.4.8. The Effect of pH in the Adsorption ........................................................................ 33
2.4.9. The Effects of Competing Ions ................................................................................ 34
2.4.10. Electrochemistry and thermodynamics of Copper dissolution .............................. 34
2.4.11. Adsorption ............................................................................................................. 36
2.4.12. Summary ................................................................................................................ 37

3. CHAPTER 3: MATERIALS AND METHODS ................................................................ 38

INTRODUCTION .............................................................................................................. 38

3.1. MATERIALS ................................................................................................................ 38

3.2. METHODS .................................................................................................................... 39

3.2.1. Ore Analysis ............................................................................................................ 40
3.2.2. Adsorption Methodology ....................................................................................... 50
3.2.3. Data Interpretation ................................................................................................. 51

4. CHAPTER 4: RESULTS AND DISCUSSION ................................................................. 52

INTRODUCTION .............................................................................................................. 52

4.1. ORE CHARACTERIZATION ....................................................................................... 52

4.1.1. Chemical Composition ......................................................................................... 52
4.1.2. Mineralogical Phase ............................................................................................... 53
4.1.3. Ore Morphology ..................................................................................................... 54

4.2. LEACHING EXPERIMENTS .................................................................................... 55

4.2.1. Chemical Analysis of Arsenic Recovery in the Pregnant Leach Solution ......... 55
4.2.2. Effect of Molar Concentration on Arsenic Adsorption .................................. 56
4.2.3. Effects of Adsorbent Dosage on Arsenic Adsorption ...................................... 60
4.2.4. Effects of Temperature on Arsenic Adsorption ................................................... 61
4.2.5. Chemical Analysis of Copper Recovery in the Pregnant Leach Solution ...... 63
4.2.6. Effect of Molar Concentration on Copper Dissolution ................................ 65
4.2.7. Effect of Adsorbents Dosage on Copper Dissolution .......................................... 66
4.2.8. Effect of Temperature on Copper Dissolution ..................................................... 67
4.2.9. Chemical Analysis of Iron in Pregnant Leach Solution .................................... 68
4.2.10. Effect of Molar Concentration on Iron Dissolution ......................................... 69
4.2.11. Effect of Adsorbents Dosage on Iron Dissolution ............................................. 70
4.2.12. Effects of Co-Existing Constituents .................................................................... 71
4.3. ARSENIC ADSORPTION

4.4. ADSORPTION MODEL

5. CHAPTER 5: CONCLUSION

REFERENCES

APPENDIX 1

APPENDIX 2

APPENDIX 3

APPENDIX 4

APPENDIX 5

APPENDIX 6

APPENDIX 7
LIST OF TABLES

Table 2-1: Incidence of Arsenic Contamination and Its Effects on Human Health 27
Table 3-1: Information on the processes, activities, and equipment 39
Table 3-2: Description of experimental Procedures 41
Table 4-1: Elemental analysis of ore sample using XRF analytical equipment 52
Table 4-2: Elemental Analysis of Ore Sample Using AAS Equipment 53
Table 4-3: Elemental analysis of a Selected Phase as displayed by the SEM EDS 56
Table 4-4: Arsenic Recovery and % As Removal obtained after Leaching 55
Table 4-5: Arsenic Recovery and % As Removal obtained at varying temperature using 1.5M sulphuric acid lixiviant 56
Table 4-6: Copper Recovery after final characterization using ICP-MS 64
Table 4-7: Copper Dissolution obtained at varying temperature using 1.5M sulphuric acid lixiviant after final characterization using ICP-MS 64
Table 4-8: Iron Dissolution and % Removal after final characterization using ICP-MS 68
Table 4-9: Iron Dissolution and % Removal obtained at varying temperature using 1.5M sulphuric acid lixiviant after final characterization using ICP-MS 69
Table 4-10: Elemental Analysis of Residue of Samples A1, A2, A3, A4 and A5 73
Table 4-11: Elemental Analysis of Residues of B1, B2, B3, B4 and B5 74
Table 4-12: Elemental Analysis of Residues of A6, A7, A8, A9, B6, B7, B8 and B9. 75
Table 4-13: Elemental Analysis of Residues of T1, T2, T3, T4, T5, T6, T7, T8, T9 and T10. 76
Table 4-14: Adsorption Data for Cerium Nanoparticles Adsorbent 76
Table 4-15: Adsorption Data for Lanthanum Nanoparticles Adsorbent 81
Table 4-16: Adsorption Data for Cerium Nanoparticles Adsorbent 81
LIST OF FIGURES

Figure 2-1: Eh-pH Diagram of Copper 35
Figure 2-2: Eh-pH Diagram of Arsenic at 25oC 36
Figure 3-1: Flow Chart of Research Experimental Set up 39
Figure 4-1: XRD Pattern of the Sample Ore showing Associated Minerals of highest Occurrence 54
Figure 4-2: Micrographs of Ore Sample Using SEM-EDS Equipment 54
Figure 4-3: Plot of Sulphuric Acid Molar Concentration (M) against Arsenic Dissolution in PLS (ppm) 56
Figure 4-4: Plot of Sulphuric Acid Molar Concentration (M) against % Arsenic Removal 57
Figure 4-5: Plot of Adsorbents Dosage (g/L) against % Arsenic Removal 60
Figure 4-6: Plot of Temperature (°C) against Arsenic Dissolution in PLS (ppm) 61
Figure 4-7: Plot of Temperature (°C) against % Arsenic Removal 62
Figure 4-8: Plot of Sulphuric Acid Molar Concentration (M) against Copper Dissolution (ppm) 65
Figure 4-9: Plot of Adsorbents Dosage (g/L) against Copper Dissolution (ppm) 66
Figure 4-10: Plot of Temperature (°C) against Copper Recovery (ppm) 67
Figure 4-11: Plot of Sulphuric Acid Molar Concentration (M) against % Iron Removal 70
Figure 4-12: Plot of Adsorbents Dosage (g/L) against % Iron Removal 71
Figure 4-13: % Adsorption in Samples where Lanthanum Nanoparticle Adsorbent is used 78
Figure 4-14: % Adsorption in Samples where Cerium Nanoparticle Adsorbent is used 79
Figure 4-15: Comparative Chart of % Adsorption Obtained when Lanthanum and Cerium Nanoparticles Adsorbents are Used 80
CHAPTER 1: INTRODUCTION

1.1. BACKGROUND

The mineral industry is a key industry on which most of human civilization stands. It has played crucial roles in human existence. The history of human civilization is the history of solid minerals. It is the story of the development of natural resources. Mineral resources development is so essential that the different ages of human civilization were named after minerals, metals or metal products: Stone Age (before 4000BC), the Bronze Age (4000 to 5000 BC), the Iron Age (1500 to 1945AD), the Nuclear Age and the Information Communication Technology Age (1945 to present) [1].

Various activities of mining, mineral processing and extraction releases arsenic into the environment. South Africa, the United States of America, Chile, Mexico, Zimbabwe, Canada, and Ghana are examples of countries where arsenic have been studied and confirmed to contaminate groundwater and soil [2]. Arsenic reportedly associates with over 300 minerals; the common source of arsenic pollution are copper and gold minerals. The metallurgical processing of concentrates of arsenic containing minerals have been adjudged to results in a more expensive cost of production, product purity deterioration and environmental hazards [3].

Copper mining dominate metalliferous mining and, on the average, it consumes over 1.3 billion m$^3$ of water attracted by mining globally in 2006 as reported by [4] when the industry was booming. The projected increase of copper demands and copper production by 3 to 21 times its current status in less than 100 years as estimated by [5] will definitely mean an increase in the required water for the different activities necessary in copper mining and processing. Rocks containing copper exposes different heavy metals when excavated, the application of water in the different activities carried out along the process of extracting copper contaminate the water with heavy metals such as selenium, lead, chromium, zinc, cadmium, mercury, manganese, nickel, arsenic, tellurium, molybdenum among other deleterious metals. This will pose a serious challenge for the increasing global population in decades to come. Copper minerals also contains different trace impurities as proven by past and contemporary researchers that can be transported into the water surrounding the mines and more virulently contaminate the groundwater which constitute
an average of 50% of global drinking water [6]. Several studies have been reported on the consequences water pollution from mining related activities have on the environment and human health by [7]–[9]

Arsenic - a major heavy metal released into the environment during mining and mineral extraction – has emerged as a source of serious concern as it threatens the human salubrity and environmental sustainability. Different researchers have investigated the presence and effects of arsenic in waters and lakes around mines or villages surrounding mines [10]. Sprague et al [11] reported the presence of high arsenic concentration in lakes surrounding a selected silver, cobalt and copper mines with samples range of 4.4 to 185 mg/kg arsenic concentration. In another study, [12] studied 207 men of non-Amerindian descent of the North of Chile exposed to arsenic in the copper-mines for a period of 19.78 ± 0.60 years. The analysis reports of the population show a total mean urinary arsenic content of 91.26 ± 6.36 ppb, the content reported ranges from 1.40 ppb to 625.20 ppb, contingent upon their job description.

Arsenic in its different species exist in oxidation state as arsenic (0), arsenite (+III), arsine (-III), and arsenate (+V). The quantity of arsenic in the solution and the oxidation state of the arsenic determines the removal of arsenic from an aqueous solution. Bulk of the techniques available for the removal or precipitation of arsenic in extractive metallurgy are used in hydrometallurgy. The process largely depends on the quantity of arsenic in the solution and the species of arsenic present [3]. Numerous studies have developed and applied different adsorbents to control arsenic pollution especially in waste water and other aqueous solution. The common adsorbents previously studied include, activated alumina, maghamite, zeolites, sepiolite, anionic clays, laterite, activated carbon and other novel adsorbents [13]–[17]. However, the application of rare earth elements impregnated compound has proven to be more effective in adsorbing arsenic from aqueous solution. Lanthanum impregnated compound have been used as an adsorbents in the removal or precipitation of arsenic from different aqueous solutions by [10], [18]–[21] while Cerium nanoparticles impregnated compound have been applied by [22]–[26] in the adsorption of arsenic from different aqueous medium.

This research focuses on the use of lanthanum and cerium nanoadsorbents for the immobilization of arsenic from the hydrometallurgical extraction of copper. In order to accomplish this goal,
copper oxide ore was leached, Lanthanum and Cerium nano adsorbents were added, different parameters such as acid molarity, temperature and adsorbents dosage were varied; and the best fitting adsorption model was studied for each of the nano adsorbents.

1.2. RESEARCH PROBLEM STATEMENT

The release of trace impurities and heavy metals into the environment through water and air from mining and mineral processing/extraction activities has attracted different policies to reduce the hazardous effects. Air pollution is said to carry different impurities which can be deleterious to health of different living organisms and the global environment. United States EPA reportedly aims at the prevention of 230 000 cases of adult mortality and 2.4 million cases of asthma by the year 2020 due to its Clean Air Act. In lieu of this, the economic disadvantage of air pollution cannot be overlooked; implementing the Clean Air Act in the United States of America alone is estimated to be $65 billion. Different countries have varying policies they have implemented in reducing the hazardous effect of air pollution; this is an important reason for seeking substantial improvement in mining activities that have proven to be one of the key causes of air pollution; this is as a result of activities such as land clearing and tree removals, excavation, drilling, communion, ore sorting, ore loading and truck movement across the site. Key emissions recognized to have been common to mining activities include: Carbon monoxide, carbon dioxide, photochemical oxidants, hydrocarbons, Methane and particulate matters which entails the heavy metals and trace impurities [6].

The position of the World Health Organizations has also underscored the adverse effect of air pollution on human health and its dire level of threat it poses to human life. Zeng et al [27] associated 470 000 premature deaths per annum globally by respiratory complications with anthropogenic ozone, he also reconciled 2.1 million deaths with anthropogenic PM2.5- comprising 7% lung cancer and 93% cardiopulmonary diseases. The consumption of air pollution containing trace impurities has been reported to bring about reduction of life expectancy by an average of eight months and some days [6].

In addition, water is also ineluctable. It is used in different activities of mining and mineral extraction processes including recovery, ore concentration, concentrates and gangues transportation, washing and several other domestic activities of mine workers. However, it is well reported that these activities - especially the ones that allows used water to flow directly or
indirectly into the environment, nearby rivers or into the ground - also affect water(streams)/well surrounding mines and the underground mines water as well. The report of [28] estimated global water usage in mining to within 2 to 4.5% of all water usage, especially in nations of the world where intensive mining activities perpetually occurs. [6] reported around 7 to 9 billion m³ of mining water usage per annum. Acid mines drainage, leaching, erosion, tailings dams’ failure and improper waste water disposal were identified as the prevailing causes of mining water pollution. Arsenic release into the environment is more prevalent with pyrometallurgical processing of copper. This is due to complex techniques of capturing gas and dust, technicalities of separation and the stability of arsenic compounds. Strict environmental regulations have been proposed in different countries and this has initiated the suggestion of the application of hydrometallurgical processes to ease the complexities involved in managing pyrometallurgical arsenic control processes [10], [29]. Almost all the techniques available for arsenic removal in the metallurgical industries are used in hydrometallurgy.

This research acknowledges the problem of increasing arsenic contamination in the environment because of mining and extraction activities. A clear problem identified is the contamination of streams, well, lakes and underground waters in mines environs. If successful, the findings of this research will offer potential solution to the problems of concentrate and tailings containing arsenic which have most often led to worrisome state of health for both humans and other living organisms.

1.3. RESEARCH QUESTIONS
Based on the different considerations, motivation and research problem statement; it is expedient to formulate four explicit research questions in line with the objective of the research:

1. How is the chemical composition and mineralogical assemblage relatable to the recovery of copper and adsorption of arsenic from the process?
2. How does Lanthanum (III) hydroxide and Cerium (IV) hydroxide behave in the leaching of copper oxide ore?
3. What is the quantity of arsenic adsorbed by the nano adsorbents at different acid molarity and adsorbent dosage?
4. Which of the nano adsorbents best fit the existing adsorption isotherm models?
1.4. **RESEARCH OBJECTIVES OF THE STUDY**

The main aim of this study is to demonstrate a line of producing a less hazardous effluent during leaching of copper.

The general objectives of the research are:

1. To perform a Mineralogical Characterization of the low-grade copper oxide ore.
2. To perform leaching experiments using sulphuric acid lixiviant.
3. To dissolve Lanthanum and Cerium nano adsorbents in the leaching experiment.
4. To Study the adsorption quantity and relate to existing adsorption model.

1.5. **RESEARCH MOTIVATION**

The research was motivated by the increasing demand in the production and consumption of copper globally which suggests an increase in arsenic contamination as result of the numerous mining activities and extraction of copper. The hazardous effects of arsenic on human health and environment emphasized the relevance of this study.

The application of rare earth nano adsorbents in the adsorption of arsenic from different aqueous solutions including water by different researchers motivated the study of the efficiency of Lanthanum and Cerium nano adsorbents in the hydrometallurgical processing of copper oxide ore.

Instead of solely relying on previous and contemporary findings of researchers; this research has been carried out in an exploratory and investigatory manner which gives an outcome that is relatable to stakeholders in different industries, academics and the government for further exploration and eventual application.

1.6. **SIGNIFICANCE OF THE STUDY**

The key significance of the research is to reduce the environmental hazards brought about by the contamination of the underground water, nearby stream/rivers and vegetation in communities surrounding mines where coppers are being leached.

To the best of our knowledge, the study of the reduction of arsenic from hydrometallurgical processing of copper ores using Lanthanum (III) hydroxide and Cerium (IV) hydroxide during have not been recorded in any literature.
1.7. **RESEARCH METHODOLOGY**

The research applies the conventionally established mineral processing and leaching methodology. The ore sample was analyzed qualitatively and quantitatively. The ore was then leached in a sulfuric acid lixiviant during which the adsorbents were added. Time of leaching and stirring speed were adopted from previous studies while acidity and adsorbent dosage were varied in this study to determine the behavior of Lanthanum (III) hydroxide and Cerium (IV) hydroxide adsorbents with different parameters.

Analyses were carried out using the X-ray fluorescence instrument, Atomic Adsorption Spectrometer and Induced Coupled Plasma instrument. The results obtained were interpreted and plotted using Microsoft excel. The adsorption model of Langmuir isotherm model was employed to study the adsorption in different forms. Different formulas were used to obtain, the quantity of adsorption, concentration of adsorption and adsorption percentage.

1.8. **DELIMITATION**

The major limitation encountered during this study is the grade of the ore. The copper oxide ore procured is of very low copper percentage, but we have proceeded to use the ore in this study since the objective of the research is to determine the adsorption capacity of Lanthanum (III) hydroxide and Cerium (IV) hydroxide in the hydrometallurgical processing of copper oxide/carbonate minerals.

The mineralogical phase experiment and ore morphology could not reveal the copper and arsenic phases in the ore. However, low detection analytical equipment was used to characterize the ore to obtain accurate composition of the ore.

1.9. **STRUCTURE OF DISSERTATION**

The introductory chapter of this dissertation started with the background of the study in which the role of copper mining in air and water pollution were clearly spelt out and the criticality of their effects on human health and the environment were emphasized. Spotlight was also beamed at the research problems, stating the current situation, the ideal situation and the solution the study aims to proffer. The research objectives were listed and the motivations behind the research were stated thereafter. The significance of the study was highlighted before going on to describe the method
employed. The study however did not go without encountering some limitations which were explained.

Chapter two presents the discussion of relevant literature in relation to the materials and methods adopted in the third chapter of the dissertation. The practicalities, significance of methods and justification of methods adopted in the execution of the experimental setup were also presented in the second chapter of the dissertation.

Chapter three reports the numerous materials used in the accomplishment of the research objectives and their sources; the list of equipment and the laboratories were also presented in this chapter.

Chapter four presents the different data obtained from the experiments carried out, plotting and interpretation of data as well as the explicit discussion of the result obtained in the experiment. The different adsorption models were reported in line with the Langmuir isotherm adsorption models.

Chapter five present the conclusions and recommendations. The chapter also present the different challenges that might have distorted the data obtained and the limitations of the research therefore making obvious research gaps and recommendations for further investigations.

Appendices were added to provide more data represented by figures in chapter four. Photos from the laboratory during the experiment were also included to show the experimental setup.
CHAPTER 2: LITERATURE REVIEW

2.1. OCCURRENCE OF COPPER MINERALS

Copper is reported to average 58 ppm in the earth crust. Chalcopyrite is the most abundant copper ore with an average percentage concentration of 34.5%. Other ores of copper which occur in magmatic, metamorphic and sedimentary rocks in different copper ore deposit worldwide include, cubanite, bornite, covellite, chalcocite, enargite, luzonite, famatinite, cuprite, malachite, azurite, chrysocolla, dioptase, atacamite, olivenite, libethenite, vandate and brochantite [30].

2.1.1. Petrology and Microscopy of Copper Minerals

Identification and characterization of ore minerals aid the process of establishing an efficient beneficiation system. Examination of an untreated ore enables the assessment of the feasibility of using density, magnetic, or electrical methods of separation, since such properties are well characterized for most minerals [31]. Previous studies have been carried out on different copper ores using microscopy. [32] used an electron microscope to study the microstructure of copper in his work on the studies of the physiology of microorganisms associated with leaching of copper. Also, [33] used a reflected light microscopy to confirm the buffer assemblage of the different structures in their work on copper partitioning between silicate melts and amphibole: experimental insight into magma evolution leading to porphyry copper ore formation. However, this experiment will employ the use of scanning electron microscopy, this is in agreement with the opinion of [34] that scanning electron microscopy reveals texture that cannot be observed by optical microscopy. The microscopy is meant to reveal the texture of the ore and that of the leached residue in this study.

2.1.2. Characterization

a. Atomic Adsorption Spectroscopy (AAS) is an efficient chemical analysis technique that can measure the content of elements. AAS can measure to as much as parts per billion of a gram (µg dm$^{-3}$) per sample owing to its efficiency [35]. Copper ore or compound has been characterized by different researchers using the AAS. In addition, [36]–[38] have all used the atomic adsorption spectroscopy to carry out chemical analysis of different compound of which copper element, arsenic and other elements were detected.

b. X-ray Fluorescence
X-ray fluorescence (XRF) spectrometer has an advantage of ease of sample preparation, stability and ease of use of x-ray spectrometer [39]. In previous studies, the use of XRF has been employed in the chemical analyses of different copper ores. It is the technique preferred by most petrologists and geochemists to obtain chemical content of the rock. The XRF is rapid and does not require special training or years of experience by the analyst [40]. Some of the similar works that have employed the use of XRF in the analysis of malachite and other copper ores include the different studies by [41] on his study on ‘X-ray fluorescence analysis of malachite ore concentrates in the Narman region’; Castro et al [42] also worked on malachite using XRF while [43] determined binding site and binding mechanism of malachite reacted with bovine serum albumin using this technique. It explicitly states the procedure and techniques for measuring the rapid and accurate content of copper in different ores using the XRF. It was however concluded that XRF is a good equipment for the quantitative examination of the copper concentrate, 0 – 2.9% was identified as the minimum concentration of copper ore to be considered economically for extraction. The use of XRF will be relevant in this study as it will help in the understanding of the chemical composition of the ore [44].

c. X-ray Diffraction
The procedure involved in the use of x-ray diffraction in the determination and identification of minerals was described by [45]. The ability of the technique to identify the nature of the substance was also stated. However, other works have been carried out using x-ray diffraction and this has brought about conviction on the use of x-ray diffraction in this study. Also, [46] applied XRD for similar experiment in their study carried out on malachite. The work of [47] cannot be overlooked also as it covers trace elements contained which constitute a part of this research.

2.2. PROCESSING OF COPPER ORE
An important stage of copper ore beneficiation is mineral separation. In this stage, the valuable minerals known as the concentrate is separated from the tailings which are not of use. The exploitation of different properties such as physical and chemical properties are taking cognizance of in the adoption or design of a separation process. However, the various separation techniques can be further read and reviewed in [48].
2.3. LEACHING OF COPPER ORE

Posiech [49] identified two metallurgical extraction categories: hydrometallurgical processing and pyrometallurgical treatment as the extraction processes developed so far. Pyrometallurgical process employ the use of high temperature chemical reactions to extract copper from its ores and concentrate; and are generally used with copper sulfides and in some cases, high grade oxides [50]. Hydrometallurgical processes however involve the dissolution of ore in an aqueous solution in a process called leaching. In a research in Nchanga, [48] stated that oxidized copper flotation was always inefficient; thereby stating this as a reason why flotation should not be considered paramount in the processing and extraction of copper from oxidized and carbonate ore. This informs the reason for the selection of hydrometallurgical method in this study.

Pyrometallurgical and hydrometallurgical techniques are the major extraction methods for copper ores. However, hydrometallurgical method has been used for a limited percentage of total copper production globally but have proven to be more environmentally friendly and technically effective especially with rigorous research going on in this area.

Leaching and other hydrometallurgical processes were first applied to copper [51]. Biswas [50] defined copper leaching as using aqueous solution for the dissolution of copper minerals. Ochromowicz [52] noted that appropriate separation processes are applied after the purification of solutions. Ammonia and sulphuric acid have been identified as the most widely used lixiviants for copper leaching. Alkaline glycine, phosphoric acid, hydrofluoric acid, nitric acid, among others have all been used to dissolve copper from of its minerals. [53]–[57]

The selection of lixiviant and process conditions is based on the type of materials and the mineralization of the ore. This informs the effectiveness of the extraction of the elements to the solution and the avoidance of emission of hazardous or toxic gases to the atmosphere.

In this study, sulphuric acid lixiviant was used to leach copper oxide ore with aim of comparatively studying the adsorption of arsenic on two different adsorbents – Lanthanum (III) hydroxide and Cerium (IV) hydroxide. The already established leaching parameters by [58], [59] and [55] will be used in carrying out the experiment. [60] identified the disadvantage of sulphuric acid as a lixiviant in a copper oxide ore containing a high percentage of calcium and magnesium owing to the high solubility of their carbonate in acid.
2.4. ARSENIC, ENVIRONMENTAL IMPACTS AND ADSORPTION

2.4.1. Chemistry of Arsenic

The chemistry of arsenic in biological systems and environment is a very complex one [61]. Arsenic is a metalloid and it exist in two forms namely: organic and inorganic [62]. Soluble arsenic in its inorganic form is usually more toxic than the soluble organic arsenic [63]. Arsenic is denoted by ‘As’ and it is found on the third row and group 5 of the periodic table. It is the 33rd element in the periodic table. The history of arsenic cannot be separated from pollution and it is a major source of environmental concerns [64]. The occurrence of arsenic has been reported in three allotropic forms which include black arsenic, metallic arsenic (grey) and yellow arsenic [65]. Arsenic reportedly ranks 20th among other trace elements in relation to their presence in the earth crust [66], it ranks 12th among the trace elements in the human body and 14th in seawater [63]. It spreads everywhere in the environment despite a 0.0001% crustal abundance in the earth [67]. The presence of arsenic is reported in more than 300 minerals and an approximate value of 5mg/L of arsenic is said to be present on earth [3].

Arsenic has excess electrons and unfilled orbital. It stabilizes within the oxidation states of -3 and +5. In its neutral state, the electronic configuration of arsenic is [Ar] 3d10s2 4p3. The configuration of arsenic permits the release of five valence electrons to chemical bonding [68]. The valence of arsenic brings about a possible formation of arsine (-3), arsenic (0), arsenite (+3) and arsenate (+5) [3]. Arsenic toxicity is a function of its valence state, arsenite is more toxic than arsenate while arsine exhibits greater toxicity than both [69].

2.4.2. Ecological Impacts of Arsenic

Arsenic accrues in living tissues by passing out very slowly in living organisms when ingested. The presence of microorganisms in the environment contributes extensively to the biogeochemistry of arsenic. A couple of reactions such as reduction, oxidation, demethylation and methylation occur between arsenic and different microorganisms. In a less volatile way than sulphur, arsenic contributes through transforming microbial from its oxidation state of +3 (arsenite) to +5 (arsenate). The possibility of reducing or oxidizing arsenic of 0 and -3 oxidation states by biochemical reactions mediation was suggested. [67].
Biological activities bring about biomethylation of arsenic in soil-water. In the course of biomethylation, there is a sediment water interface between the activities of fungi (including *Candida humicola* and *Aspergillus glaucus*) and that of bacteria (including *Flavobacterium* sp, *Escherichia coli*, *Methanobacterium* sp, among others) [70]. The toxicological effects, the biological availability and physiological arsenic toxicity in the environment all is proportional to its chemical form. The ecological impact of arsenic depends on the reducing potential of arsenic and the reducing potential of the environment where it occurs [63].

2.4.3. Environmental Effects of Arsenic and Other Trace Impurities

The importance of this study can be further established when the role of arsenic and other trace elements contamination on human health is considered. The role of mining operations in contaminating the soil with toxic trace elements is often not taken seriously enough or neglected. Remote areas accounts for most of these activities, this likely explains why they are often overlooked. Large heaps of unused gangues are abandoned, the Sulphur in some of the gangue minerals causes acidic leaching when oxidized or exposed to water. Toxic elements are mobilized by this acidity and are washed to sensitive locations where water and soil are being polluted [71].

Herder [72] reported arsenic as an harmful element to multi-cellular life. Mining and mineral processing activities accounts for the increasing presence of arsenic in the environment. 50µg/L was identified by World Health Organization as the tolerable amount of arsenic in drinking water. This corresponds with the position of the United States Environmental Protection Agency on the standard arsenic content in drinking water. Meanwhile, failure of important organs such as lungs, kidney, liver, bladder as a result of cancer linked to arsenic contamination has been reported to be in the range of 1 to 13 of 1000 people. EPA and WHO standard and maximum content allowed was unable to stop this mortality rate [73]. In the report of [73], a more detailed permissible content was reported as follow: a range of 80 to 250 µg/kg range of normal arsenic level in hair, 5 to 40 µg/day normal arsenic content in urine and a range of 430 to 1080 µg/kg range of normal arsenic level in nail. The result from the different studies reported by [73] shows different complications resulting from arsenic presence greater than the permissible content. A study of 200 villages in West Bengal over a period of 10 years registered 4,420 (15.02%) villagers from 151 villages of 29, 035 people from the studied 200 villages. The registered people were suffering with arsenic induced skin lesions. In a similar manner, a total of 2,736 (24.47%) from 112 villages of 11, 180
people from 118 villages were registered in Bangladesh. The study reported 6 months to 2 years as the duration it most likely takes for the symptomatology of arsenic toxicity to develop harmfully. Different symptoms were recorded and the most prominent ones include rough dry skin, spotted pigmentation, nodular or diffuse keratosis on the sole of the foot and palm; leucomelanosis, diffuse melanosis, gums, lips; conjunctiva congestion, splenomegaly, solid edema, hypatomegaly, ascites [73].

2.4.4. Effects of Arsenic Contamination on Human Health

Numerous mining activities contaminate the water and air surrounding copper mines with major trace impurities including arsenic. These impurities pose to be a cause of concern especially with respect to human health and environmental sustainability. Different studies have been carried out on arsenic presence in waters and lakes around mines or villages surrounding mines [12], [74]–[83]. Sprague et al [11] reported the presence of high concentration of arsenic in lakes surrounding a selected silver, cobalt and copper mines with samples range of 4.4 to 185 mg/kg arsenic concentration. In another study, [12] studied 207 men from the North of Chile in contact with arsenic in the copper-mines for a period of 19.78 ± 0.60 years. The analysis reports of the population show a total mean urinary arsenic content of 91.26 ± 6.36 ppb, the content ranges from 1.40 ppb to 625.20 ppb, contingent upon their job description. In that study, the author was able to establish a positive correlation between the Arsenic (III) methyltransferase change and the frequency of micronucleus. Their finding agreed with the established role of the Arsenic (III) methyltransferase enzyme in arsenic methylation. He therefore assumed that the fraction of the population with variant allele will accrue bigger quantity of a more toxic monomethylarsonic acid which will then result into a higher frequency of cytogenetic damage.

The effect of arsenic contamination on human health have been reported in different studies including: [12], [74]–[83]. Studies of arsenic effect on animal health has also been carried out by [84], [85]. Bjørklund [86] pointed out the linkages of chronic inorganic arsenic exposure to diverse kinds of cancers and various other pathological consequences in humans collectively referred to as arsenicosis. It was however concluded that Arsenic-Induced (As-in) epigenetic modifications have the potential to interrupt cellular homeostasis which often results into the modulation of key tracts in the carcinogenesis induced by Arsenic.
Furthermore, most drinking water contaminated by arsenic and other toxic metals serves as a source of drinking for the remote areas hosting the mines especially in Africa and some developing countries across the world. The contamination of these drinking water by toxic elements especially Arsenic is a great concern worldwide [87]. An association of this contamination with serious biological and social consequences throughout the world was established in that study. Meanwhile, [87] further identified arsenic toxicity as an unfortunate reason for protein energy deficiency (PED) and chronic energy deficiency (CED) which are strongly linked to increasing arsenic carcinogenesis. It was also noted to alter various cellular processes and interrupting the interactivity between steroid receptors and their DNA response elements. Hence, Arsenic increases cell proliferation by producing keratinocyte-derived growth factor (KGF) [87].

Oggianno et al. [88] established the linkage between trace elements (like Pb and selenium) and a neurodegenerative disorder known as Amyotrophic lateral sclerosis (ALS). While [89] studied the association between trace elements and stroke. His conclusion establishes the effect of selenium on increasing stroke. He was unable to posit the linkage between Arsenic and Stroke but [90] revealed a role for arsenic in ischemic stroke. In addition, [91] highlighted the environmental effects of arsenic in groundwater in the causes of stroke and other cardiovascular diseases.

The adverse effects of arsenic and other trace impurities on human health and other living organisms are well enumerated in the following studies [12], [24], [26], [74], [79], [81], [82], [92]–[94]. The different incidence of chronic arsenic poisoning and its effects on human health are displayed in Table 2-1.
### Table 1-1: Incidence of Arsenic Contamination and Its Effects on Human Health

<table>
<thead>
<tr>
<th>S/N</th>
<th>Incidence</th>
<th>Resulting Health Complications</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Taiwan (1961 – 1985)</td>
<td>Chronic arsenicism, hyperpigmentation, keratosis, cancer (liver, bladder, skin, lung, prostate, kidney)</td>
<td>[63], [95]–[97]</td>
</tr>
<tr>
<td>2.</td>
<td>Mexico (1963 – 1983)</td>
<td>Skin cancer, keratosis, skin pigmentation changes, gastrointestinal disturbances, peripheral vascular disease.</td>
<td>[98]–[100]</td>
</tr>
<tr>
<td>3.</td>
<td>Antofagasta, Chile (1959 – 1970)</td>
<td>Raynaud's syndrome, mesenteric arterial thrombosis, ischemia of the tongue, myocardial ischemia, arsenicism, acrocyanosis.</td>
<td>[63], [101], [102]</td>
</tr>
<tr>
<td>4.</td>
<td>West Bengal-India (1978 – 1980s)</td>
<td>Arsenicosis</td>
<td>[73], [83], [103]–[105]</td>
</tr>
<tr>
<td>5.</td>
<td>Ontario, Canada (1930s)</td>
<td>Arsenic dermatosis</td>
<td>[106]</td>
</tr>
<tr>
<td>7.</td>
<td>Argentina (1955)</td>
<td>Endemic arsenical skin disease, skin cancer, bladder cancer.</td>
<td>[17], [110], [111]</td>
</tr>
<tr>
<td>8.</td>
<td>China (1980s)</td>
<td>Arsenicosis, fluorosis, arsenicism, keratosis,</td>
<td>[63], [112]–[114]</td>
</tr>
</tbody>
</table>
leucoderma or melanosis on the skin, cardiac infarction and/or bronchitis, gangrene

<table>
<thead>
<tr>
<th></th>
<th>Location</th>
<th>Syndrome or Disease</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.</td>
<td>Millard County, Utah, USA (1970s)</td>
<td>Prostate cancer, hypertensive heart disease, nephrosis, and nephritis.</td>
<td>[115]–[117]</td>
</tr>
<tr>
<td>10.</td>
<td>Bangladesh</td>
<td>Arsenicosis, skin cancer, pigmentation, keratosis</td>
<td>[73], [81], [103], [118]–[120]</td>
</tr>
<tr>
<td>11.</td>
<td>Poland (1898)</td>
<td>Skin cancer</td>
<td>[17], [63], [121], [122]</td>
</tr>
<tr>
<td>12.</td>
<td>Northern India</td>
<td>Extra hepatic portal vein obstruction, non-cirrhotic portal fibrosis and cirrhosis.</td>
<td>[123], [124]</td>
</tr>
</tbody>
</table>

2.4.5. Effect of Arsenic Contamination on Animals

Animals have contact with arsenic than an average human, they consume arsenic from drinking water, feedstuff, vegetables, leaves and grasses. The consumption of arsenic has been found to be a major cause of inorganic chemical poisoning of animals [84]. Arsenic is retained in the different discharge such as blood, defecation, urine, hair and tissues of these animals; this retained arsenic can be passed on to humans also when the affected animal is consumed. The use of dungs of an affected animal also makes the possibility of arsenic pollution higher. Pal et al. [125] studied the contamination rate of arsenic in villages at Ganga-Meghna-Brahmaputra plains located in India. Cow dungs are used as fuel in unventilated ovens as cooking process. It was found that people consume 1859.2ng arsenic through direct inhalation and it was recorded that the respiratory tract can consume over 464.8ng arsenic.

Arsenic contamination effects on various animals have been studied. In order to observe the effects of arsenic toxicosis on Sheep, Maji et al. [126] exposed a group of Garole Sheep to oral arsenic feeding of 6.6 mg Kg\(^{-1}\) in a study that spanned through over 133 days. It was observed that the sheep tend to pass out toxic arsenic through their urine and faeces. However, a gradual accumulation of arsenic was observed in the wool of the arsenic exposed Garole Sheep. 0.80 mg
Kg\(^{-1}\) to 3.4 mg Kg\(^{-1}\) was found to be the range of arsenic content in the hair of cattle, the range observed from the findings reconciles with the assertions of [127].

In farm animals, the detection of arsenic in urine, milk and faeces becomes possible in about 10 days after the consumption of contaminated material [128]. The rate at which the animal urinates is affected and arsenic can be as high as 16 mg Kg\(^{-1}\) in a large volume of urine. Arsenic might however be low in milk ranging from 0.25mg Kg\(^{-1}\) to 1.5 mg Kg\(^{-1}\) for cows depending on the period of consumption and the acuteness of poisoning. Deposition of arsenic on animal’s hair remains until the hair is removed and this deposition can range from 5 mg Kg\(^{-1}\) to 10 mg Kg\(^{-1}\). Arsenic contamination is also reported to have degenerative effects on the kidneys and livers of animals affected by arsenic toxicosis. A detection of 10 to 15 mg Kg\(^{-1}\) arsenic trioxide in the liver or kidney should be viewed as a diagnosis of arsenic toxicosis. The life of the animal can be cut short if the hepatic level of the animal cannot measure up to the contamination [128].

Arsenic contamination also poses a grave threat to the aquatic animals. The cytotoxicity of exposing fish cell lines to sodium arsenite have been established by [85], [129]. Moreover, [129] treated two fish cell lines with sodium arsenite to compare the cytotoxicity induced by arsenic in different fish cells. Both fish cells lines – Therapon jarbua fin cells and Tilapia ovary cells – were treated for 2 hours with arsenite of high concentration (20 - 160µM) and 24 hours with arsenite of low concentration (0.125 - 10µM). It was found out that the fin cells of Therapon jarbua were induced with apoptosis from the reaction with sodium arsenite, oxidative stress was however suggested to have resulted from the reaction. The resulting oxidative stress was concluded to disturb the ovary cells of the Tilapia. It was established that the progression of cell cycles can be disrupted by arsenic. In some cases, as evident in [129] experiment, arsenic is capable of inducing apoptosis in the cells while in some other cases, it drastically reduces the rate of survival of the cells by disturbing the cell cycles which might make the cell go through necrosis.

Other species of fishes have been used in the study of arsenic effects on the aquatic animals. The study of Rainbow trout (Oncorhynchus mykiss) in a pair-fed growth investigation established the growth impairment caused by exposure to arsenic. In a period of 17 weeks, the fishes were exposed to 0.0 mg arsenite·L\(^{-1}\), 0.76 mg arsenite·L\(^{-1}\), 2.48 mg arsenite·L\(^{-1}\), and 9.64 mg arsenite·L\(^{-1}\). The fishes exposed to over 9.64 mg arsenite·L\(^{-1}\) had a reduced growth rate by 55%. It was found out
that the reduction in growth was primarily as a result of reduced appetite and likely a direct metabolic impact. The study showed that the gallbladder wall was inflamed for all fishes exposed to over 9.64 mg arsenite-L$^{-1}$. The threshold established for chronic arsenic toxicity was reported as 4.9 mg L$^{-1}$ [130].

2.4.6. Immobilization of Arsenic in Aqueous Solution: Application in Hydrometallurgical Extraction of Copper

Arsenic species exists in oxidation state such as arsenic (0), arsenite (III), arsine (-III) and arsenate (+V). Adsorption capability is largely connected to the oxidation state of the arsenic and quantity of arsenic present in the solution. The most effective arsenic removal state was reported to be the pentrivalent oxidation state. [3], [131].

The metallurgical processing of concentrates of arsenic containing minerals have been adjudged to results in a more expensive cost of production, product purity deterioration and environmental hazards [3]. Arsenic release into the environment is more prevalent with pyrometallurgical processing of copper. This is due to complex techniques of capturing gas and dust, technicalities of separation and the stability of arsenic compounds. Strict environmental regulations have been proposed in different countries and this has initiated the suggestion of the application of hydrometallurgical processes to ease the complexities involved in managing pyrometallurgical arsenic control processes [29]. Almost all the techniques available for the immobilization of arsenic in the metallurgical industries are used in hydrometallurgy. The process largely depends on the quantity of arsenic in the solution and the species of arsenic present. Arsenic oxidation is the first step required in the immobilization of arsenic, the oxidations helps in the stability of the precipitates [3]. Air and oxygen were identified as basic oxidants for arsenic in alkaline solutions [131]. However, the use of air and oxygen have been limited due to their low oxidation rate and stronger oxidants such as ozone, hypochlorite, chlorine hydrogen peroxide, and a mixture of SO$_2$/O$_2$ gases are recommended for a better reaction kinetics [3], [132].

In the case of low grade copper ores, heap leaching and dump leaching have been the conventional methods of leaching since the early 1900s. Application of bioleaching is more prevalent for this technique of copper extraction [133]. The method of oxidation in this kind of leaching technique is that of biological oxidation in which chemical species are oxidized by microbial mechanisms. It
is an indirect method of oxidation in which microorganisms oxidizes ions like ferrous to ferric which eventually serves as oxidants for other species [3].

Pentavalent oxidation state has been identified as the most suitable state for the removal of arsenic notwithstanding the method adopted. Arsenate and arsenite are both soluble in water, but the tendency to precipitate out of aqueous solution when metal cation is added is higher for arsenate. The precipites’ stability however depends on the kind of metal cation added to the solution [134].

The popular methods of immobilizing arsenic from copper aqueous solution during hydrometallurgical extraction include (a) lime neutralization – precipitating arsenic as calcium arsenate and/or calcium arsenite at a pH within 11 an 12 [135].

(b) Sulphide Precipitation – example is the leaching of the arsenic containing concentrate using Na₂S at 80 – 105°C with NaOH also present during this process. In order to separate the resulting arsenic free concentrate from Sodium thioarsenate, crystallization is carried out by evaporating, cooling and filtration. Different procedures have been applied for sulphide precipitation of arsenic bearing concentrates [136].

(c) Co-precipitating with Ferric ions – This entails the addition of ferric ions to the solution to precipitate the arsenic. Li et al [137] added 0 to 12g of pyrite to a solution containing 200g lead copper matte with 7/92% Arsenic content. The addition of pyrite generated ferric ions to precipitate arsenic in the leaching liquid. Arsenic content of 0.25g/L was achieved at 10g dosage of pyrite. It was concluded to be the first successful application of ferric ion (through the addition of pyrite) to precipitate arsenic in a lead copper matte liquid leaching. The concept of coprecipitating arsenic with ferric ions is to neutralize the Fe (III) ions bearing solution to produce a phase of ferric oxyhydroxide known as ferrihydride. The adsorption of anions and cations including AsO₄³⁻ is done by the ferrihydride adsorbent [138]. The demonstration of the method have been reviewed by [131].

(d) Encapsulation Technology – In this technique, arsenic bearing pollutants in the form of large blocks or small particles are isolated in an inert compound with structural integrity. The surface of the deleterious metals exposed to the leaching solution is minimized and the toxic material is eventually dissolved. Manganese dioxide has been used as natural oxidizer at a temperature
between 50 °C – 100 °C, calcium hydroxide is then added to form calcium arsenate before the addition of either of sodium oxide, sodium carbonate, silica, alumina, feldspar or calcium oxide to the residue of calcium arsenate. The mixture is heated within 1000 °C – 1200 °C [3], [139], [140].

e) Precipitation of trace elements from tailings (Arsenic) using Lime and Barium Chloride

Moon, Dermatas and Menounou, (2004) applied the use of lime in precipitating calcium-arsenic from treated soil. He was able to conclude that precipitation increases with increasing calcium-arsenic molar ratio. However, Harper and Kingham, (1992) employed the use of hydrated lime and ferric chloride to remove over 99% of original arsenic from waste water. Other studies in which lime was used to precipitate arsenic from soil or waste water include Jia and Demopoulos, (2008) and Gupta and Chen, (1978). In addition, Weir and Masters, (1982) demonstrated the possibility of using barium chloride to obtain barium arsenate by reducing the pH of the solution to about 10.

2.4.7. Adsorption of Arsenic from Copper Oxide leaching solution

Adsorption is defined as the concentration of an element or compound on a surface or at an interface. It is a reaction between two or more surfaces including: gas and solid; gas and liquid; liquid and liquid; and liquid and solid [145].

Numerous studies have developed and applied different adsorbents to control arsenic pollution especially in waste water and other aqueous solution. The common adsorbents previously studied include activated alumina, zeolites, sepiolite, maghamite, anionic clays, activated carbon laterite and other novel adsorbents [13]–[17]. However, the application of rare earth elements impregnated compound has proven to be more effective in adsorbing arsenic from aqueous solution. Lanthanum impregnated compound was used as an adsorbents in the immobilization or precipitation of arsenic from different solutions by [18]–[21] while Cerium nanoparticles impregnated compound have been applied by (Feng et al. 2018; L. Zhang et al. 2016; Li et al. 2012; He, Tian, and Ning 2012) in the adsorption of arsenic from different aqueous medium.

Jang et al. [92] identified Lanthanum as one of the cheapest rare-earth elements. Its non-toxicity and environment friendliness were also noted. Lanthanum impregnated SBA-15 was employed to absorb arsenic from sodium arsenate (Na$_2$HAsO$_4$·7H$_2$O, Sigma). A better adsorption of arsenic was obtained using Lanthanum-impregnated SBA-15 than when activated alumina was used.
Reichel et al. [146] carried out a co-precipitation technique for the separation of trace impurities such as selenium, arsenic, antimony, bismuth, tin, iron, lead and tellurium from blister copper. Lanthanum oxide was used in an ammoniacal solution of copper nitrate. The trace impurities of As, Sb, Te and Se were removed at pH above 9.0. He established the potential of Lanthanum hydroxide for advance separation and concentration of massive sample of copper and macrocomponent not precipitating in ammonium hydroxide.

Guo [18] identified the different adsorbents researched in the past for the control of arsenic pollution. He identified iron based layered double hydroxide as a promising adsorbent for arsenic immobilization due to the high affinity of iron hydroxides for arsenic; he however concluded that rare earth elements – especially La based compounds – including Lanthanum hydroxide and Lanthanum oxide have shown a better ability to mobilize arsenic from aqueous solution. The result of his experiment showed a highly efficient adsorbent for arsenic removal in aqueous solution especially with increasing Lanthanum in the Layered doubled hydroxide.

Deng et al. [147] successfully used Cerium fibrous protein (CeFP) to get rid of fluoride, phosphate and arsenate from aqueous solutions. Increasing adsorption of arsenate from solution till pH 3.0 then constancy in the adsorption rate from 3.0 to 7.0 before decreasing with further increase in the pH of the solution was reported.

Herder [72] developed a Cerium-oxide coated alumina adsorbent to investigate the immobilization of arsenic from ground water. The current arsenic removal technique was identified as economically unviable for adsorbing arsenic from aqueous solution. Also reported that Cerium-oxide coated alumina performs than uncoated alumina at any pH. It was established that a better adsorbing capacity at a lower temperature than when the temperature is increased. This may be due to the ability of Cerium dioxide coated alumina to sinter at a high temperature.

2.4.8. The Effect of pH in the Adsorption

The pH is expected to determine if the unionized or ionized species will remain in the solution. It will also determine the degree of ionization of the precipitates [145]. In a solvent containing phosphate ions, iron and manganese hydroxides, an increase in pH will engender better adsorption of arsenic onto the adsorbents.
2.4.9. The Effects of Competing Ions

Increase in the quantity of cations and anions adsorbed onto the surfaces bring about a change to surface precipitation from mononuclear adsorption. Arsenic is intimately related to manganese and iron hydroxides/oxides presence in a solution.

During adsorption, the ions present in the solution tend to compete with the adsorption of arsenic on the adsorbent. Arsenic adsorption has been mostly affected by the following anions in the given order:

phosphate > selenite > citrate > tartrate > malate > oxalate > sulfate > selenate.

It was however reported that the efficiency of these anions to prevent arsenic adsorption from an aqueous solution decreases with increasing pH [148]. Decreasing pH gives phosphate a high tendency to join the coordination sheath iron (III) ions.

The similarity of phosphate anions to arsenate ions and its high affinity for metal oxides makes it compete with arsenate ions during adsorption. High level of silicate and carbonate also has effects on arsenic adsorption rate but the effect on arsenic immobilization is minor [145].

2.4.10. Electrochemistry and thermodynamics of Copper dissolution

The knowledge of Pourbaix diagram is a prerequisite in order to efficiently establish the interaction between surface area/porosity of the molecules and the adsorbents properties.

Pourbaix diagram can be defined as a 2D representation of a multi-dimensional space (pH, temperature, potential, and concentration- among others). Potential-pH diagram which is the most common Pourbaix diagram is described by an aqueous solution environment, plotting of potential on an axis and pH on the other axis and composition of a gaseous specie, liquid constituent and dissolved solid.

The Eh-pH diagram of copper is displayed in Figure 2-1.
Pourbaix Diagram of Arsenic

Panagiotaras [150] described the chemistry of arsenic in aqueous solution. In aqueous solution, arsenic reportedly shows anionic behavior. In sulphide minerals, the derivatives of arsenic and arsine will most probably take place under extreme reduction condition provided that the pH is low. Environmental conditions have great influence on the valence state of arsenic. The pH is particularly a huge factor. Other factors include: redox potential, sulphur presence, calcium, iron, microbial activities, and complex ions presence. However, adsorption and desorption reactions will most likely alter the behaviour of arsenic in aqueous solutions.

Half reaction of the reduction from As(V) to As(III) as given by [150] is captured in Equation 1:

\[
H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O
\]

Equation 1

\[
E = E^\circ + k \left[ \log_{10} \left( \frac{[As(V)]^{a^{p}}}{[As(III)]^{a^{III}}} \right) - 2pH \right]
\]

Equation 2

Equation 2 was derived to relate the concentrations of As (III) and As (V) with the equilibrium redox potential of the pH. Figure 2-2 present the Eh-pH diagram of arsenic.

Figure 2-1: Eh-pH Diagram of Copper [149]
However, the presence of organic matter dictates the effects of microorganisms on the adsorption reaction involving arsenic in an aqueous solution. These organic ligands are liable of joining with arsenic or decrease the adsorption capacity. The ability to apply the knowledge of the behaviour of arsenic in different aqueous solutions under different conditions will solve a lot of environmental and biological problems.

2.4.11. Adsorption

Chemical and physical processes take place at different interfaces. Adsorption occurs in different systems and it finds application in laboratory research and the industry. The quantity of substance adsorbed is a function temperature, vapor pressure and surface area. Other important nature of the reagents and nature of adsorbents plays significant role in the adsorption experiment.

**Adsorption Mechanism**

The stages of adsorption mechanism include:

a. the diffusion of adsorbate on the surface of the adsorbents

b. movement into the adsorbent pores

c. buildup of monolayer of the adsorbate on the adsorbent

![Figure 2-2: Eh-pH Diagram of Arsenic at 25°C](image-url)
**Adsorption Isotherm**

This refers to the relationship existing between the adsorbed amount equilibrium and the pressure at a constant temperature. The imbalance attractive forces existing at the surface are reduced by adsorption thereby forming a heterogeneous system surface free energy.

2.4.12. Summary

Considering the efforts of numerous researchers in immobilizing arsenic from various aqueous solutions using rare earth nano adsorbents as reviewed, the focus of this study is therefore to investigate the use of rare earth nano adsorbents especially Lanthanum and Cerium nano adsorbents to immobilize arsenic from copper aqueous solution during its hydrometallurgical processing. The project adopt the methodology, results, discussion and conclusion of different studies to adopt the use of sulphuric acid lixiviant to leach copper out of the ore sample while simultaneously studying the surface chemistry between Lanthanum and Cerium nano adsorbents and arsenic and other competing ions present in the system.
CHAPTER 3: MATERIALS AND METHODS

INTRODUCTION
Chapter three presents the different materials procured to facilitate the successful execution of this research. The second section of the chapter explains the procedure of the experiment carried out to obtain the various results presented in chapter four. The design of this research methodology was deduced from the conclusions, assertions and recommendations obtained from the literature review. The methodology was designed towards the analysis of the low-grade copper ore; leaching of the ore in sulphuric acid lixiviant; application of Lanthanum (III) hydroxide and Cerium (IV) hydroxide adsorbents to selectively separate arsenic from the copper aqueous solution and analyzing the data.

3.1. MATERIALS
The materials used in the research include low grade copper ore, adsorbents, sulphuric acid lixiviant, deionized water, nitric acid and laboratory apparatus. The two adsorbents used in this research are Lanthanum Hydroxide and Cerium Hydroxide. Low grade copper ore was procured from the Democratic Republic of Congo; Lanthanum hydroxide and Cerium hydroxide were procured from Sigma-Aldrich, Modderfontein, Johannesburg, South Africa (reference no: 8204970406) and sulphuric acid and nitric acid were procured from Associated Chemicals Enterprises (PTY) Limited (reference number: 75405). De-ionized water was used throughout the study. Aside the raw materials and the reagents to be used in this research, other equipment and apparatus was used with respect to the phase of the research and the nature of the process as contained in Table 3-1.
Table 3-1: Information on the processes, activities, and equipment

<table>
<thead>
<tr>
<th>Process</th>
<th>Activity/Study</th>
<th>Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore Analysis</td>
<td>Ore Microscopy</td>
<td>SEM (EDS)</td>
</tr>
<tr>
<td></td>
<td>Chemical/Elemental</td>
<td>AAS</td>
</tr>
<tr>
<td></td>
<td>Analysis</td>
<td>XRF</td>
</tr>
<tr>
<td>Leaching and Adsorption</td>
<td>Acid Leaching</td>
<td>Laboratory Apparatus (Beakers,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Measuring Cylinder)</td>
</tr>
<tr>
<td>Final Characterization</td>
<td>Chemical Analysis</td>
<td>ICP-MS and AAS</td>
</tr>
<tr>
<td>Data Analysis</td>
<td>Results Plotting and</td>
<td>Microsoft Excel</td>
</tr>
<tr>
<td></td>
<td>Analysis</td>
<td></td>
</tr>
</tbody>
</table>

3.2. METHODS

The flowchart of the experimental setup is presented in Figure 3-1.

Figure 3-1: Flow Chart of Research Experimental Set up
3.2.1. Ore Analysis

a. **X-Ray Fluorescence**

10g of the ore sample was weighed using the weighing balance and then mixed thoroughly with 2g of Sasol wax. The mixture was mounted and heated at 50 °C for 10 minutes. XRF (ZSX Primus II) was used in analyzing the sample to obtain the chemical constituents of the ore.

b. **Atomic Adsorption Spectroscopy**

Atomic Adsorption Spectrometer (Model - ICE 3300 Serial No - C103300198) equipped with Cu-Zn-Mn-Fe lamp, Al and As lamp was used in analyzing the ore sample. 10g of the ore sample was weighed into a 400ml beaker, 25 mL concentrated HCl was added; the mixture was cover and placed on a medium hot plate. 15 mL was added after 15 minutes after which digestion was allowed for 20 minutes. 25 mL HCl and 25 mL de-ionized water were then added respectively. The beaker was covered and boiled to dissolve all soluble salts and eliminate nitric acid digestion gases. The mixture was cooled and diluted into 100 mL de-ionized water before being filtered for analysis. Air-acetylene gas flame was used in carrying out the analysis. Arsenic, Copper, Iron, Magnesium and Aluminium concentration were determined.

3.2.2. Leaching and adsorption experiments

A total of 28 leaching experiments were carried out. H$_2$SO$_4$ was used in the first set of 18 experiments. The molar concentration of sulphuric acid in the process was varied between 0.5, 1, 1.5, 2 and 3. Lanthanum hydroxide dosage of 0.2 g/L was added in each of the set of molar concentrations. The dosage of Lanthanum hydroxide was then varied from 0.2g/L to 0.1 g/L, 0.4g/L, 0.6 g/L and 0.8 g/L. The leaching and adsorption could take place for 3 hours and the Pregnant Leached Solution (PLS) was filtered through No. 2 Whatman filter paper into a flask with screw cap. ICP-MS was used to detect the concentration of arsenic, iron and copper in the PLS and the tailings left from the filtration. The same procedure was repeated when Cerium hydroxide was applied as an adsorbent. Another set of experiment was also carried out to vary the temperature between 25 °C to 80 °C.

All samples contain 30g of low-grade copper ore sample mixed with sulphuric acid lixiviant. In samples A1, A2, A3, A4 and A5, H$_2$SO$_4$ lixiviant concentration was varied as 0.5, 1, 1.5, 2 and 3 respectively with an addition of 0.2g/L lanthanum nano adsorbent dosage while B1, B2, B3, B4
and B5 has the same lixiviant variation but with 0.2g/L Cerium nano adsorbent dosage. A6, A7, A8 and A9 have a fixed H2SO4 lixiviant concentration of 1.5M while the lanthanum nano adsorbent dosage was varied as 0.1g/L, 0.4g/L, 0.6g/L and 0.8g/L respectively and B6, B7, B8 and B9 retained a fixed H2SO4 concentration of 1.5M but a varied cerium nano adsorbent as 0.1g/L, 0.4g/L, 0.6g/L and 0.8g/L respectively. ICP-MS was used to analyze the pregnant leached solution while the residues were characterized using XRF. T1, T2, T3, T4 and T5 contains 0.2g/L lanthanum hydroxide nano adsorbent at a varying temperature of 25, 40, 50, 65 and 80°C respectively. While T6, T7, T8, T9 and T10 contains 0.2g/L cerium oxide nano adsorbent at a varying temperature of 25, 40, 50, 65 and 80°C respectively.

During the leaching and adsorption reactions, the solution was agitated using a magnetic stirrer at a speed of 150 rpm and the time adopted for each set of experiment was 3 hours. The solution was covered during the process to avoid constant air bubbling. Modification of the leaching medium through continuous sampling was prevented by loading each set - with same original content but varied parameters - at once. The sets were withdrawn after three hours and were immediately filtered and analyzed using the ICP-MS and AAS. The experimental setup of the 28 samples is presented in Table 3-2.

Table 3-2: Description of experimental Procedures

<table>
<thead>
<tr>
<th>S/N</th>
<th>Experiment</th>
<th>Procedure</th>
</tr>
</thead>
</table>
| 01. | Sample A1 | a. 30g of the ore sample was weighed  
30g of ore sample + H2SO4  
+ Lanthanum (III) Hydroxide  
*A  
|     |            | b. Sulfuric acid lixiviant was used  
c. Experiment was carried out at 3 molar concentration  
d. 0.2 g/L Lanthanum adsorbent was used  
e. Pregnant Leached Solution was filtered out of the mixture  
f. Precipitates were also prepared for analysis  
g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF  |
| 02. | Sample A2 | a. 30g of the ore sample was weighed  
b. Sulfuric acid lixiviant was used  
c. Experiment was carried out at 2 molar concentration  |
| Sample | 30g of ore sample + $\text{H}_2\text{SO}_4$ + Lanthanum (III) Hydroxide | 03. Sample A3  
30g of ore sample + $\text{H}_2\text{SO}_4$ + Lanthanum (III) Hydroxide | a. 30g of the ore sample was weighed  
b. Sulfuric acid lixiviant was used  
c. Experiment was carried out at 1.5 molar concentration  
d. 0.2 g/L Lanthanum adsorbent was used  
e. Pregnant Leached Solution was filtered out of the mixture  
f. Precipitates were also prepared for analysis  
g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF |
|---|---|---|---|
| Sample | 04. Sample A4  
30g of ore sample + $\text{H}_2\text{SO}_4$ + Lanthanum (III) Hydroxide | a. 30g of the ore sample was weighed  
b. Sulfuric acid lixiviant was used  
c. Experiment was carried out at 1 molar concentration  
d. 0.2 g/L Lanthanum adsorbent was used  
e. Pregnant Leached Solution was filtered out of the mixture  
f. Precipitates were also prepared for analysis  
g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF |
| Sample | 05. Sample A5  
30g of ore sample + $\text{H}_2\text{SO}_4$ + Lanthanum (III) Hydroxide | a. 30g of the ore sample was weighed  
b. Sulfuric acid lixiviant was used  
c. Experiment was carried out at 0.5 molar concentration  
d. 0.2 g/L Lanthanum adsorbent was used |
<p>| | | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td></td>
<td>Sample A6</td>
<td></td>
</tr>
</tbody>
</table>
|   | 30g of ore sample + H$_2$SO$_4$ + Lanthanum (III) Hydroxide | e. Pregnant Leached Solution was filtered out of the mixture  
   f. Precipitates were also prepared for analysis  
   g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF |
| 06. |   | a. 30g of the ore sample was weighed  
   b. Sulfuric acid lixiviant was used  
   c. Experiment was carried out at 1.5 molar concentration  
   d. 0.1 g/L Lanthanum adsorbent was used  
   e. Pregnant Leached Solution was filtered out of the mixture  
   f. Precipitates were also prepared for analysis  
   g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF |
|   | Sample A7 |   |
|   | 30g of ore sample + H$_2$SO$_4$ + Lanthanum (III) Hydroxide | a. 30g of the ore sample was weighed  
   b. Sulfuric acid lixiviant was used  
   c. Experiment was carried out at 1.5 molar concentration  
   d. 0.4 g/L Lanthanum adsorbent was used  
   e. Pregnant Leached Solution was filtered out of the mixture  
   f. Precipitates were also prepared for analysis  
   g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF |
| 07. |   | a. 30g of the ore sample was weighed  
   b. Sulfuric acid lixiviant was used  
   c. Experiment was carried out at 1.5 molar concentration  
   d. 0.6 g/L Lanthanum adsorbent was used  
   e. Pregnant Leached Solution was filtered out of the mixture  
   f. Precipitates were also prepared for analysis  
   g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF |
|   | Sample A8 |   |
|   | 30g of ore sample + H$_2$SO$_4$ + Lanthanum (III) Hydroxide |   |
|   |   | e. Pregnant Leached Solution was filtered out of the mixture  
|   |   | f. Precipitates were also prepared for analysis  
|   |   | g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF  
| 09. | Sample A9  
|   | 30g of ore sample + H₂SO₄ + Lanthanum (III) Hydroxide | a. 30g of the ore sample was weighed  
|   | | b. Sulfuric acid lixiviant was used  
|   | | c. Experiment was carried out at 1.5 molar concentration  
|   | | d. 0.8 g/L Lanthanum adsorbent was used  
|   | | e. Pregnant Leached Solution was filtered out of the mixture  
|   | | f. Precipitates were also prepared for analysis  
|   | | g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF  
| 10. | Sample B1  
|   | 30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide | a. 30g of the ore sample was weighed  
|   | | b. Sulfuric acid lixiviant was used  
|   | | c. Experiment was carried out at 3 molar concentration  
|   | | d. 0.2 g/L Cerium adsorbent was used  
|   | | e. Pregnant Leached Solution was filtered out of the mixture  
|   | | f. Precipitates were also prepared for analysis  
|   | | g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF  
| 11. | Sample B2  
|   | 30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide | a. 30g of the ore sample was weighed  
|   | | b. Sulfuric acid lixiviant was used  
|   | | c. Experiment was carried out at 2 molar concentration  
|   | | d. 0.2 g/L Cerium adsorbent was used  
|   | | e. Pregnant Leached Solution was filtered out of the mixture  
|   | | f. Precipitates were also prepared for analysis  

**B**
<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Description</th>
<th>Analysis Details</th>
</tr>
</thead>
</table>
| 12. | B3      | 30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide | a. 30g of the ore sample was weighed  
b. Sulfuric acid lixiviant was used  
c. Experiment was carried out at 1.5 molar concentration  
d. 0.2 g/L Cerium adsorbent was used  
e. Pregnant Leached Solution was filtered out of the mixture  
f. Precipitates were also prepared for analysis  
g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF |
| 13. | B4      | 30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide | a. 30g of the ore sample was weighed  
b. Sulfuric acid lixiviant was used  
c. Experiment was carried out at 1 molar concentration  
d. 0.2 g/L Cerium adsorbent was used  
e. Pregnant Leached Solution was filtered out of the mixture  
f. Precipitates were also prepared for analysis  
g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF |
| 14. | B5      | 30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide | a. 30g of the ore sample was weighed  
b. Sulfuric acid lixiviant was used  
c. Experiment was carried out at 0.5 molar concentration  
d. 0.2 g/L Cerium adsorbent was used  
e. Pregnant Leached Solution was filtered out of the mixture  
f. Precipitates were also prepared for analysis  
g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF |
<table>
<thead>
<tr>
<th></th>
<th>Sample B6</th>
<th></th>
<th>Sample B7</th>
<th></th>
<th>Sample B8</th>
<th></th>
<th>Sample B9</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>15.</td>
<td>30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide</td>
<td>a. 30g of the ore sample was weighed</td>
<td>16.</td>
<td>30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide</td>
<td>a. 30g of the ore sample was weighed</td>
<td>17.</td>
<td>30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide</td>
<td>a. 30g of the ore sample was weighed</td>
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<td></td>
<td></td>
<td>b. Sulfuric acid lixiviant was used</td>
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<td>b. Sulfuric acid lixiviant was used</td>
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<td>b. Sulfuric acid lixiviant was used</td>
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<td>c. Experiment was carried out at 1.5 molar concentration</td>
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<td>c. Experiment was carried out at 1.5 molar concentration</td>
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<td>c. Experiment was carried out at 1.5 molar concentration</td>
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<td></td>
<td></td>
<td>d. 0.1 g/L Cerium adsorbent was used</td>
<td></td>
<td></td>
<td>d. 0.4 g/L Cerium adsorbent was used</td>
<td></td>
<td></td>
<td>d. 0.6 g/L Cerium adsorbent was used</td>
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<td></td>
<td></td>
<td>e. Pregnant Leached Solution was filtered out of the mixture</td>
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<td>e. Pregnant Leached Solution was filtered out of the mixture</td>
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<td>e. Pregnant Leached Solution was filtered out of the mixture</td>
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<td>f. Precipitates were also prepared for analysis</td>
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<td>f. Precipitates were also prepared for analysis</td>
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<td>f. Precipitates were also prepared for analysis</td>
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<td></td>
<td>g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF</td>
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<td></td>
<td>g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF</td>
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<td></td>
<td>g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF</td>
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<tr>
<td>18.</td>
<td></td>
<td>a. 30g of the ore sample was weighed</td>
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<tr>
<td>Sample</td>
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</tr>
</tbody>
</table>
| T1     | 30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide | a. 30g of the ore sample was weighed  
  b. Sulfuric acid lixiviant was used  
  c. Experiment was carried out at 1.5 molar concentration  
  d. 0.8 g/L Cerium adsorbent was used  
  e. Pregnant Leached Solution was filtered out of the mixture  
  f. Precipitates were also prepared for analysis  
  g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF |
| T2     | 30g of ore sample + H₂SO₄ + Lanthanum (III) Hydroxide | a. 30g of the ore sample was weighed  
  b. Sulfuric acid lixiviant was used  
  c. Experiment was carried out at 1.5 molar concentration and 25°C  
  d. 0.2 g/L Lanthanum adsorbent was used  
  e. Pregnant Leached Solution was filtered out of the mixture  
  f. Precipitates were also prepared for analysis  
  g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF |
| T3     | 30g of ore sample + H₂SO₄ + Lanthanum (III) Hydroxide | a. 30g of the ore sample was weighed  
  b. Sulfuric acid lixiviant was used  
  c. Experiment was carried out at 1.5 molar concentration and 40°C  
  d. 0.2 g/L Lanthanum adsorbent was used  
  e. Pregnant Leached Solution was filtered out of the mixture  
  f. Precipitates were also prepared for analysis  
  g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF |
<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>22. T4</td>
<td>30g of ore sample + H₂SO₄ + Lanthanum (III) Hydroxide</td>
<td>c. Experiment was carried out at 1.5 molar concentration and 50°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d. 0.2 g/L Lanthanum adsorbent was used</td>
</tr>
<tr>
<td></td>
<td></td>
<td>e. Pregnant Leached Solution was filtered out of the mixture</td>
</tr>
<tr>
<td></td>
<td></td>
<td>f. Precipitates were also prepared for analysis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF</td>
</tr>
<tr>
<td>23. T5</td>
<td>30g of ore sample + H₂SO₄ + Lanthanum (III) Hydroxide</td>
<td>a. 30g of the ore sample was weighed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b. Sulfuric acid lixiviant was used</td>
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<tr>
<td></td>
<td></td>
<td>c. Experiment was carried out at 1.5 molar concentration and 65°C</td>
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<tr>
<td></td>
<td></td>
<td>d. 0.2 g/L Lanthanum adsorbent was used</td>
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<tr>
<td></td>
<td></td>
<td>e. Pregnant Leached Solution was filtered out of the mixture</td>
</tr>
<tr>
<td></td>
<td></td>
<td>f. Precipitates were also prepared for analysis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF</td>
</tr>
<tr>
<td>24. T6</td>
<td>30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide</td>
<td>a. 30g of the ore sample was weighed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b. Sulfuric acid lixiviant was used</td>
</tr>
</tbody>
</table>
25. **Sample T7**

30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide

<p>| | | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>25.</td>
<td>Sample T7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>a.</strong></td>
<td>30g of the ore sample was weighed</td>
<td></td>
</tr>
<tr>
<td><strong>b.</strong></td>
<td>Sulfuric acid lixiviant was used</td>
<td></td>
</tr>
<tr>
<td><strong>c.</strong></td>
<td>Experiment was carried out at 1.5 molar concentration and 40°C</td>
<td></td>
</tr>
<tr>
<td><strong>d.</strong></td>
<td>0.2 g/L Cerium adsorbent was used</td>
<td></td>
</tr>
<tr>
<td><strong>e.</strong></td>
<td>Pregnant Leached Solution was filtered out of the mixture</td>
<td></td>
</tr>
<tr>
<td><strong>f.</strong></td>
<td>Precipitates were also prepared for analysis</td>
<td></td>
</tr>
<tr>
<td><strong>g.</strong></td>
<td>Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF</td>
<td></td>
</tr>
</tbody>
</table>

26. **Sample T8**

30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>26.</td>
<td>Sample T8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>a.</strong></td>
<td>30g of the ore sample was weighed</td>
<td></td>
</tr>
<tr>
<td><strong>b.</strong></td>
<td>Sulfuric acid lixiviant was used</td>
<td></td>
</tr>
<tr>
<td><strong>c.</strong></td>
<td>Experiment was carried out at 1.5 molar concentration and 50°C</td>
<td></td>
</tr>
<tr>
<td><strong>d.</strong></td>
<td>0.2 g/L Cerium adsorbent was used</td>
<td></td>
</tr>
<tr>
<td><strong>e.</strong></td>
<td>Pregnant Leached Solution was filtered out of the mixture</td>
<td></td>
</tr>
<tr>
<td><strong>f.</strong></td>
<td>Precipitates were also prepared for analysis</td>
<td></td>
</tr>
<tr>
<td><strong>g.</strong></td>
<td>Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF</td>
<td></td>
</tr>
</tbody>
</table>

27. **Sample T9**

30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>27.</td>
<td>Sample T9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>a.</strong></td>
<td>30g of the ore sample was weighed</td>
<td></td>
</tr>
<tr>
<td><strong>b.</strong></td>
<td>Sulfuric acid lixiviant was used</td>
<td></td>
</tr>
</tbody>
</table>
Experiment was carried out at 1.5 molar concentration and 65°C
d. 0.2 g/L Cerium adsorbent was used
e. Pregnant Leached Solution was filtered out of the mixture
f. Precipitates were also prepared for analysis
g. Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF

<table>
<thead>
<tr>
<th>28.</th>
<th>Sample T10</th>
</tr>
</thead>
<tbody>
<tr>
<td>30g of ore sample + H₂SO₄ + Cerium (IV) Hydroxide</td>
<td></td>
</tr>
</tbody>
</table>

| a. | 30g of the ore sample was weighed |
| b. | Sulfuric acid lixiviant was used |
| c. | Experiment was carried out at 1.5 molar concentration and 80°C |
| d. | 0.2 g/L Cerium adsorbent was used |
| e. | Pregnant Leached Solution was filtered out of the mixture |
| f. | Precipitates were also prepared for analysis |
| g. | Analysis was carried out on the PLS and the precipitates using ICP-MS, AAS and XRF |

* A – Experiment with Lanthanum nano adsorbents; **B – Experiment with Cerium nano adsorbents and ***T – Experiment where temperature is varied

3.2.2. Adsorption Methodology

The adsorption of arsenic from the leaching solution was carried out by preparing series of adsorbents ranging from 0.1g/L to 0.8g/L at a constant molar concentration of 1.5. A 20-milligram mass of the prepared dosage was dispersed into 100 ml leaching solution. The flasks were placed on a shaking reactor to ensure that equilibrium is reached, and the different constituents are thoroughly mixed. The precipitated constituents were then filtered, dissolved and digested for analysis using ICP-MS to detect residual As (V).

The amount of adsorption from the solution was calculated as:

\[ q_e = \frac{(c_0 - c_e)V}{m} \] (1)
Where: $Q_e$ is the amount of adsorption

$C_0$ is the initial concentration

$C_e$ is the concentration at time $t$,

$V$ is the volume of the solution and

$M$ is the mass of the sorbent

The analyses of adsorption data were carried out using the Langmuir and Freundlich adsorption isotherms models.

**Langmuir Adsorption Model:** The nonlinear Langmuir model was obtained using the following expression:

$$q_e = q_m K_L \frac{C_e}{1 + K_L C_e}$$

Where, $q_m$ (mg/g) is the maximum adsorption capacity

$q_e$ (mg/g) is the equilibrium adsorption capacity

$C_e$ (mg/L) is the equilibrium constant

$K_L$ (L/mg) is the Langmuir adsorption constant

$C_e$ and $K_L$ are both related to the capacity of adsorption and net enthalpy of adsorption. To determine $K_L$, the graph of $C_e/q_e$ was plotted against $C_e$. From the graph, the slope was calculated, and the linear graph produced $y = mx + c$ equation.

$m = \text{intercept} = 1/q_e$. Hence, $q_e = 1/m$ and $C=1/q_m K_L$.

From the value of $C$, $K_L$ was then determined.

3.2.3. Data Interpretation

Data interpretation was done using Microsoft Excel 2010. All formulas and calculations such as slope, $r^2$ and intercept were all determined using excel built in functions.
CHAPTER 4: RESULTS AND DISCUSSION

INTRODUCTION
This chapter presents the results of the characterization carried out on the ore, the chemical analysis of the pregnant leached solution and residue obtained after leaching. The effects of acid concentration, adsorbent dosage and temperature variation were studied on the dissolution and adsorption of arsenic, copper and iron. Langmuir adsorption model was used to study the result and the best fitting nano adsorbent is presented.

4.1. ORE CHARACTERIZATION

4.1.1. Chemical Composition

In Table 4-1, Elemental Analysis of the ore sample using the XRF analytical equipment is presented.

Table 4-1: Elemental analysis of ore sample using XRF analytical equipment

<table>
<thead>
<tr>
<th>S/N</th>
<th>Constituents</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na</td>
<td>1 288</td>
</tr>
<tr>
<td>2</td>
<td>Mg</td>
<td>21 406</td>
</tr>
<tr>
<td>3</td>
<td>Al</td>
<td>58 866</td>
</tr>
<tr>
<td>4</td>
<td>Si</td>
<td>115 741</td>
</tr>
<tr>
<td>5</td>
<td>P</td>
<td>501</td>
</tr>
<tr>
<td>6</td>
<td>S</td>
<td>10 918</td>
</tr>
<tr>
<td>7</td>
<td>Cl</td>
<td>190</td>
</tr>
<tr>
<td>8</td>
<td>K</td>
<td>5 373</td>
</tr>
<tr>
<td>9</td>
<td>Ca</td>
<td>368 649</td>
</tr>
<tr>
<td>10</td>
<td>Ti</td>
<td>6 385</td>
</tr>
<tr>
<td>11</td>
<td>Cr</td>
<td>320</td>
</tr>
<tr>
<td>12</td>
<td>Mn</td>
<td>5 283</td>
</tr>
<tr>
<td>13</td>
<td>Fe</td>
<td>22 574</td>
</tr>
<tr>
<td>14</td>
<td>Ni</td>
<td>127</td>
</tr>
<tr>
<td>15</td>
<td>Cu</td>
<td>53</td>
</tr>
<tr>
<td>16</td>
<td>Zn</td>
<td>47</td>
</tr>
<tr>
<td>17</td>
<td>As</td>
<td>24</td>
</tr>
<tr>
<td>18</td>
<td>Rb</td>
<td>38</td>
</tr>
<tr>
<td>19</td>
<td>Sr</td>
<td>817</td>
</tr>
<tr>
<td>20</td>
<td>Y</td>
<td>102</td>
</tr>
<tr>
<td>21</td>
<td>Zr</td>
<td>249</td>
</tr>
<tr>
<td>22</td>
<td>Ba</td>
<td>941</td>
</tr>
</tbody>
</table>
The result obtained from Table 4-1 shows XRF analysis with a copper content of 53ppm, arsenic content of 24ppm and iron content of 22 574ppm.

Table 4-2 presents the result of the chemical analysis carried out on the ore using the Atomic Adsorption Spectrometer. The different element targeted during the analysis include copper, arsenic and iron.

Table 4-2: Elemental Analysis of Ore Sample Using AAS Equipment

<table>
<thead>
<tr>
<th>S/N</th>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cu</td>
<td>53.2</td>
</tr>
<tr>
<td>2.</td>
<td>As</td>
<td>24.4</td>
</tr>
<tr>
<td>3.</td>
<td>Fe</td>
<td>22335</td>
</tr>
</tbody>
</table>

The result of the AAS analysis shown in Table 4-2 displays a copper concentration of 53.2ppm, arsenic concentration of 24.4 ppm and an iron concentration of 22 335ppm. In the case of copper and arsenic, the result corresponds with that obtained from the elemental analysis carried out using the XRF as displayed in Table 4-1. However, the concentration of iron is a little lower than that obtained in Table 4-1.

Considering the method adopted in the preparation of sample in which samples were separated after final preparation of XRF sample, the difference cannot be attributed to the sample collection, handling of sample, or the preparation of sample [152]. This little variation is attributable to the result of the digestion or the analytical method itself since the equipment was able to give accurate result in other chemical components analysed [153].

4.1.2. Mineralogical Phase

The determination of the mineralogical phases using the x-ray diffraction (XRD) method shows the different gangue minerals present in the mineral sample including: quartz, quicklime (CaO), larnite (Ca₂SiO₄), hatrurite, magnetite, dolomite, calcite, wustite, hongquite, nichromite, franklinite and spine. The occurrence of well-ordered calcite is evident as shown in Figure 4-1. No traces of arsenic or copper was identified by this analysis. The inability of the X-ray diffraction method to detect copper and arsenic phases was attributed to the very low content available in the ore as shown in Table 4-1 and Table 4-2 [154] and [155].
4.1.3. Ore Morphology

The low-grade value of the ore made it difficult for the equipment to identify the copper and arsenic phases [152]. The particle size of the associated constituents had an average particle size of 400nm in diameter. The constituents show an irregular structure which can be linked to the dominance of the constituent in the mineral - calcite [156]. However, the micrograph shows that the materials are aggregated partially.
The energy dispersive spectrum (EDS) of the selected phase in Table 4-3 shows the elemental composition of the mineral; elemental phases identified in the spectrum include, Magnesium, Aluminium, Silica, Sulphur, Potassium, Manganese, Calcium, Titanium and Iron. The result was as expected since the chemical analysis carried out had shown the presence of these constituents. Copper and arsenic were not identified in the spectrum due to the minute quantity present in the ore.

Table 4-3: Elemental analysis of a Selected Phase as displayed by the SEM EDS

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Mn</th>
<th>Fe</th>
<th>Totals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight%</td>
<td>2.16</td>
<td>44.72</td>
<td>10.28</td>
<td>6.53</td>
<td>7.47</td>
<td>0.51</td>
<td>0.34</td>
<td>23.48</td>
<td>0.26</td>
<td>0.32</td>
<td>3.92</td>
<td>100.00</td>
</tr>
</tbody>
</table>

4.2. LEACHING EXPERIMENTS

4.2.1. Chemical Analysis of Arsenic Recovery in the Pregnant Leach Solution

Table 4-4 shows the arsenic recovery and percentage arsenic removal at varying parameters such as Lanthanum (III) OH Adsorbent Dosage, Cerium (IV) Oxide Adsorbent Dosage and Molar Concentration of sulphuric acid lixiviant.

Table 4-4: Arsenic Recovery and % As Removal obtained after Leaching

<table>
<thead>
<tr>
<th>Samples</th>
<th>Adsorbent Dosage (g/L)</th>
<th>Molar Concentration</th>
<th>Time (minutes)</th>
<th>Arsenic Concentration (ppm)</th>
<th>% As Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>La (III) OH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>0.2</td>
<td>3M</td>
<td>180</td>
<td>3.1987</td>
<td>86.67</td>
</tr>
<tr>
<td>A2</td>
<td>0.2</td>
<td>2M</td>
<td>180</td>
<td>3.8197</td>
<td>84.08</td>
</tr>
<tr>
<td>A3</td>
<td>0.2</td>
<td>1.5M</td>
<td>180</td>
<td>1.8216</td>
<td>92.41</td>
</tr>
<tr>
<td>A4</td>
<td>0.2</td>
<td>1M</td>
<td>180</td>
<td>0.0338</td>
<td>99.86</td>
</tr>
<tr>
<td>A5</td>
<td>0.2</td>
<td>0.5M</td>
<td>180</td>
<td>0.2516</td>
<td>98.95</td>
</tr>
<tr>
<td>A6</td>
<td>0.1</td>
<td>1.5M</td>
<td>180</td>
<td>0.6629</td>
<td>97.24</td>
</tr>
<tr>
<td>A7</td>
<td>0.4</td>
<td>1.5M</td>
<td>180</td>
<td>1.8821</td>
<td>92.16</td>
</tr>
<tr>
<td>A8</td>
<td>0.6</td>
<td>1.5M</td>
<td>180</td>
<td>0.1127</td>
<td>99.53</td>
</tr>
<tr>
<td>A9</td>
<td>0.8</td>
<td>1.5M</td>
<td>180</td>
<td>0.4346</td>
<td>99.34</td>
</tr>
<tr>
<td></td>
<td>Ce (IV) OH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>0.2</td>
<td>3M</td>
<td>180</td>
<td>0.1117</td>
<td>99.53</td>
</tr>
<tr>
<td>B2</td>
<td>0.2</td>
<td>2M</td>
<td>180</td>
<td>0.0026</td>
<td>99.99</td>
</tr>
<tr>
<td>B3</td>
<td>0.2</td>
<td>1.5M</td>
<td>180</td>
<td>0.3448</td>
<td>99.99</td>
</tr>
<tr>
<td>B4</td>
<td>0.2</td>
<td>1M</td>
<td>180</td>
<td>2.2412</td>
<td>90.66</td>
</tr>
<tr>
<td>B5</td>
<td>0.2</td>
<td>0.5M</td>
<td>180</td>
<td>0.6855</td>
<td>97.14</td>
</tr>
<tr>
<td>B6</td>
<td>0.1</td>
<td>1.5M</td>
<td>180</td>
<td>1.5471</td>
<td>93.55</td>
</tr>
<tr>
<td>B7</td>
<td>0.4</td>
<td>1.5M</td>
<td>180</td>
<td>0.8290</td>
<td>96.95</td>
</tr>
<tr>
<td>B8</td>
<td>0.6</td>
<td>1.5M</td>
<td>180</td>
<td>3.1938</td>
<td>96.69</td>
</tr>
<tr>
<td>B9</td>
<td>0.8</td>
<td>1.5M</td>
<td>180</td>
<td>3.7589</td>
<td>99.31</td>
</tr>
</tbody>
</table>
Table 4-5 display the arsenic recovery and percentage arsenic removal at varying temperature and using Lanthanum (III) OH Adsorbent and Cerium (IV) Oxide Adsorbents.

Table 4-5: Arsenic Recovery and % As Removal obtained at varying temperature using 1.5M sulphuric acid lixiviant

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adsorbent Dosage (g/L)</th>
<th>Temperature (°C)</th>
<th>Time (Minutes)</th>
<th>As Concentration (ppm)</th>
<th>% As Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>La (III) OH</td>
<td>0.2</td>
<td>25</td>
<td>180</td>
<td>1.8216</td>
<td>92.41</td>
</tr>
<tr>
<td>T1</td>
<td>0.2</td>
<td>40</td>
<td>180</td>
<td>2.8700</td>
<td>88.04</td>
</tr>
<tr>
<td>T2</td>
<td>0.2</td>
<td>50</td>
<td>180</td>
<td>2.9344</td>
<td>87.77</td>
</tr>
<tr>
<td>T3</td>
<td>0.2</td>
<td>65</td>
<td>180</td>
<td>2.4322</td>
<td>89.87</td>
</tr>
<tr>
<td>T4</td>
<td>0.2</td>
<td>80</td>
<td>180</td>
<td>2.0995</td>
<td>91.25</td>
</tr>
<tr>
<td>Ce (IV) OH</td>
<td>0.2</td>
<td>25</td>
<td>180</td>
<td>0.3448</td>
<td>98.56</td>
</tr>
<tr>
<td>T6</td>
<td>0.2</td>
<td>40</td>
<td>180</td>
<td>1.4447</td>
<td>93.98</td>
</tr>
<tr>
<td>T7</td>
<td>0.2</td>
<td>50</td>
<td>180</td>
<td>1.5275</td>
<td>93.64</td>
</tr>
<tr>
<td>T8</td>
<td>0.2</td>
<td>65</td>
<td>180</td>
<td>1.9735</td>
<td>91.77</td>
</tr>
<tr>
<td>T9</td>
<td>0.2</td>
<td>80</td>
<td>180</td>
<td>2.1765</td>
<td>90.93</td>
</tr>
</tbody>
</table>

4.2.2. Effect of Molar Concentration on Arsenic Adsorption

Figure 4-3 shows the plot of the variation of molar concentration of sulphuric acid against the concentration of arsenic dissolved in the pregnant leach solution while Figure 4-4 display the variation of sulphuric acid molar concentration plotted against the percentage arsenic removal.

Figure 4-3: Plot of Sulphuric Acid Molar Concentration (M) against Arsenic Dissolution in PLS
Figure 4-4: Plot of Sulphuric Acid Molar Concentration (M) against % Arsenic Removal

The effect of the molarity of the sulphuric acid was investigated. The molar concentrations considered during the dissolution process ranges from 0.5 to 3 molar concentration. As observed in Figure 4-3, the quantity of arsenic that was dissolved in the sulphuric acid lixiviant in the presence of Lanthanum hydroxide adsorbent showed a slight decrease from 0.5 molar concentration to 1 molar concentration before increasing from 1 molar concentration to 2 molar concentration before subsequent decrease. While with the application of Cerium hydroxide adsorbent, there was an increase in arsenic dissolution from 0.5M of sulphuric acid lixiviant to 1M before a spontaneous decrease. A direct relationship can be established between the concentration of acid and the arsenic dissolution. Basir [157] explained the reason why molar concentration of sulphuric acid affects extraction percentage of metals. The formation of metal oxide prior to sulphate was identified as the reason for the effects of molarity of sulphuric acid on the extraction percentage of metal species. In respect of the unstable values of dissolution in which the trend rises at certain values and decreases at certain values also, a similar occurrence was recorded by [58] in which acid consumption was high till 1.02 mol/L sulphuric acid before experiencing a decrease in dissolution rate. Weight loss was observed to reduce with increasing acid concentration.

The trend of % Arsenic removal with increasing molar concentration of sulphuric acid lixiviant was displayed in Figure 4-4. With the addition of Lanthanum adsorbent, a slight increase in arsenic removal was observed from 98.95% to 99.86% between 0.5mol/L to 1 mol/L sulphuric acid lixiviant concentration before a constant decrease occurred to 84.08% at 2 mol/L before subsequent increase in % arsenic removal from the process.
In a contrary manner, the addition of Cerium adsorbent resulted to decreasing % arsenic removal from 97.14% to 90.66% between 0.5 mol/L to 1 mol/L H₂SO₄ lixiviant. From 1 mol/L, an increase in arsenic removal was obtained to 99.99% at 1.5 mol/L before a constant trend of arsenic removal was obtained in the process. From Figure 4-4, it is clear that arsenic can be removed to a large extent with the application of Lanthanum and Cerium impregnated adsorbents. The % arsenic removal has been determined to range from 84.08% to 99.99% in the leaching of low-grade copper oxide ore at varying H₂SO₄ molar concentration using Lanthanum and Cerium impregnated adsorbents. However, the application of Cerium adsorbent has proven to be more effective in the removal of arsenic from the adsorption process at higher molar concentration of sulphuric acid lixiviant while Lanthanum adsorbent was able to remove more arsenic at lower sulphuric acid molar concentrations – 0.5 mol/L to 1 mol/L. In comparison, at 0.5 mol/L of H₂SO₄ lixiviant, Cerium adsorbent was able to remove 97.14% arsenic while Lanthanum adsorbent removed 98.95% arsenic; also, at 1 mol/L of H₂SO₄ lixiviant, Cerium adsorbent removed 90.66% arsenic while Lanthanum adsorbent removed 99.86% arsenic. Meanwhile, in higher molar concentrations of sulphuric acid, Cerium adsorbents removed within 99.53% to 99.99% arsenic while Lanthanum adsorbents removed from 84.08% to 92.41% arsenic. The fluctuations in the adsorption with increasing and decreasing acidity is similar to the adsorbent performance reported by [26]. This was justified by the different species of arsenic present under different concentration and pH of the lixiviant. As specified by [158], As(III) arsenic species occurs mostly as H₃AsO₃ below a pH of 9.2 but as H₂AsO₃⁻ at pH over 9.2; while As(V) occurs predominantly as negatively charged HAsO₂⁻ or H₂AsO₄⁻ in the pH range of 2.2 to 11.5. In this experiment, where a pH of less than 1 was investigated across different concentration of sulphuric lixiviant, the repulsion level is little, and adsorption continually increases with increasing molar concentration to cover all active adsorption sites; except in rare cases where co-existing ions interfered at the binding sites.

As reported by [18], the acidity of the solution affects the arsenic adsorption efficiency of the solution. Lower acidity yielded decrease in the arsenate adsorption in that experiment. This can be related to the pH value of the particles in the liquid environment when the negative charges are balanced by the sum of the positive charges on the surface. At high molar concentration of acid, the surface of the Cerium impregnated adsorbent is positively charged thereby bringing about increase in arsenic adsorption whose surface is already negatively charged. However, the presence of competing ions affected this phenomenon when Lanthanum adsorbent was added, the
adsorption of arsenic decreased with increasing acidity. Coexisting ions with higher ionic density as observed from the chemical analysis carried out will negatively affect the adsorption efficiency of arsenic in an aqueous solution as observed from the application of Lanthanum adsorbent in Figure 4-4 [18]. However, in a similar outcome, [21] reported efficient arsenic adsorption at higher acidity using Lanthanum carbonate and Lanthanum hydroxide. The research spelt out the importance of pH of the solution in determining the adsorption efficiency of the adsorbents. Lanthanum adsorbents is adjudged not to dissolve at pH ranging from neutral to alkalinity level in which hydroxide group is recommended for such adsorption.

As studied by [25], a high adsorption capacity at pH within 1 and 7 was recorded on adsorbing arsenate and arsenite on cerium loaded resin, and a sharp decrease in adsorption of arsenate and arsenite with decreasing acidity and increasing alkalinity was obtained. However, using Cerium adsorbents, [25] applauded its ability to operate at neutral and acidic pH without sacrificing its adsorption efficiency in the operation. The high percentage of arsenic adsorbed with the application of both Lanthanum and Cerium impregnated compounds adsorbents cannot be divulged from [159] conclusion that the tendency of arsenic to be adsorbed is stronger under acidic condition than under alkaline condition. The anionic arsenite and arsenate species absorbs more effectively on Cerium adsorbents with increased acidity; this is due to the abundant positive charges being possessed by the Cerium nanoparticles impregnated adsorbents at sorption sites when used at higher molar concentration of acid or low pH [25]. Also, one can associate the instability of the Cerium ions at higher acid concentration to the higher adsorption capacity unlike during lower concentration of acidity and increased alkalinity during which the adsorbent ions becomes more stable until it eventually reaches equilibrium.

The interference of co-existing ions with the adsorption of arsenate and arsenite from the process is expected; this account for the inconsistency in the trend of the plot. These ions are expected to directly compete with arsenic anions in the binding sites. Phosphate, silicate, carbonate anions and iron ions are the most likely constituents that interfered in this adsorption experiment. The efficiencies of these anions are however reduced by decreasing acidity [148]. The only exception is phosphate anions that still possess the high tendency to join the coordinating iron (III) ions during the adsorption process. This mechanism will be discussed more in subsequent sections.
4.2.3. Effects of Adsorbent Dosage on Arsenic Adsorption

In figure 4-5, the variation of adsorbent dosage of Lanthanum hydroxide and Cerium oxide is plotted against the arsenic dissolution obtained in the PLS in the former and the % arsenic removal in the later.

Figure 4-5: Plot of Adsorbents Dosage (g/L) against % Arsenic Removal

The effect of adsorbents dosage on the removal efficiency of arsenic was investigated. The outcome as observed in Figure 4-5 revealed the efficiency of adsorption of arsenic in the order of the increase in the dosage of Lanthanum adsorbent and Cerium adsorbents. It can be deduced that the process containing more La$^{3+}$ content removed more arsenic. Lesser arsenic anions bond with Lanthanum and Cerium ions at 0.1g/L adsorbent dosage; thereafter, the amount of arsenic anions bonding with Lanthanum and Cerium ions increased from 0.2g/L adsorbent dose. The bonding was constant till 0.4g/L Lanthanum impregnated adsorbent dosage, also, the constancy remains till 0.6g/L Cerium impregnated adsorbent dosage. The bonding continued to rise thereafter until 0.8g/L adsorbents dosage. This reconciles with [18] findings in which arsenate removal efficiency was discovered to increase sharply with increasing adsorbent dosage before leveling up at adsorbent dosage above 1.0g/L when Lanthanum impregnated adsorbent was used in the investigation of arsenic adsorption in an arsenate solution. Conventionally, the rate at which a solute is adsorbed is a function of the concentration of the adsorbents; this is as a result of the increase in active exchangeable active sites. Meanwhile, the overall adsorption per unit weight of
an adsorbent may diminish due to disturbance brought about by the interaction of active sites of the adsorbent [160].

The investigation did not reach the optimum adsorbent dose. Iftekhar et al [160] identified 1g/L to 2g/L as the dose in which optimum adsorbents varies for Lanthanum adsorption. Excessive dosage of adsorbents has been proven to decrease the efficiency of the adsorbents [161]. However, the optimum adsorption is generally associated with the availability of active site. Surface functional groups, coexisting ions and adsorption condition plays a major role in determining the optimum adsorption. In this research, the highest adsorption obtained was 99.34% arsenic removal at 0.8g/L dose of Cerium impregnated adsorbent. It was noteworthy that the trend of adsorption was increasing at the maximum adsorbent dosage tested, hence cannot be concluded as the optimum adsorption dosage.

4.2.4. Effects of Temperature on Arsenic Adsorption

In figures 4-6 and 4-7, the temperature of the leaching and adsorption process was varied from 25°C to 80°C in the process involving the two different adsorbents – Lanthanum hydroxide and Cerium oxide. The plot of the temperature against the arsenic dissolution is shown in Figure 4-6 and the plot of the temperature against the % arsenic removal is shown in Figure 4-7.

Figure 4-6: Plot of Temperature (°C) against Arsenic Dissolution in PLS (ppm)
The effect of increased temperature is obvious on the enlargement of the adsorbents’ interaction between the solid and liquid; and the mobility of the arsenic ions [162]. The dependency of adsorption on temperature is widely reported. The solute loading increases in most cases as the temperature increases. Thermodynamically, removal of arsenate is more likely at higher temperature than at arsenite [163].

With the addition of lanthanum adsorbents. Figure 4-6 shows arsenic adsorption reducing from 92.41% at 25 °C to 88.04% at 40 °C. A further decrease was observed at 50 °C to 87.77% before a sudden increase began to take place at higher temperature. Lanthanum nano adsorbent has an initial slower mobility of arsenic ions into lanthanum adsorbent pores before an increase in adsorption velocity with increasing temperature which consequentially caused an increase in adsorption capability with temperature increase. Also, [19] identified the increase in temperature as a cause of increment of driving force between the coexisting ions in the solution and decreases the energy barrier. Decreasing energy barrier brought about an increase in adsorption velocity with the addition of lanthanum nano adsorbent. The adsorption of arsenic was higher at elevated temperature, depicting an equilibrium state of the system whereby both ions were active, and this makes it possible for bonding to occur easily. The stronger the interaction between the two ions, the more active the ions are and the more the adsorption that occurs.

Also, with the addition of cerium adsorbents as shown in figure 4-7, decrease in arsenic adsorption was observed from 98.56% at 25°C to 93.98% at 40°C; further decrease in arsenate adsorption rate
was observed with increase in temperature. The decreasing activity of cerium ions with increasing temperature until the system was no longer at the state of equilibrium around 41°C, this explains the reason for lower adsorption at higher temperature [164]–[167].

The behavior of cerium adsorbent which emerged as the better adsorbent reconciles with the conclusion by [72], that a better adsorption of arsenic from aqueous solution using cerium oxide nanoparticles coated with alumina. For cerium adsorbent, mobility of arsenic ions was faster at lower temperature but decreased from over 41°C. In correlation with the report from a study by [168], the competition for active sites increases with temperature but adsorption velocity decreases spontaneously from 41°C, increasing adsorption velocity brings about a decrease in arsenic concentration in the leaching system and swift mobility of arsenic ions into the adsorbent pores. Also, the concentration of cerium nano adsorbents decreases with increasing temperature, hence a decreasing adsorbent molecule density which instigates segregation and rapid detachment of arsenic onto adsorbent surfaces. The active sites are almost totally saturated at low temperature (higher concentration), this describes the inhibition of further adsorption of arsenic ions onto the cerium nano adsorbents molecules surfaces beyond 41°C. However, it is more important to note that the trend of the adsorption of arsenic in different scenarios is dictated by the nature of the ore and the coexisting ions. The ability of cerium ions to adsorb arsenic better at room temperature explains the reason for its better performance in previous studies as most studies are carried out at room temperature.

4.2.5. Chemical Analysis of Copper Recovery in the Pregnant Leach Solution

Table 4-6 reveal the copper dissolution and percentage copper recovered at varying parameters such as Lanthanum (III) OH Adsorbent Dosage, Cerium (IV) Oxide Adsorbent Dosage and Molar Concentration of sulphuric acid lixiviant.
The copper dissolution and percentage copper recovered at varying temperature while using Lanthanum (III) OH Adsorbent and Cerium (IV) Oxide Adsorbents are shown in Table 4-7.

Table 4-7: Copper Dissolution obtained at varying temperature using 1.5M sulphuric acid lixiviant after final characterization using ICP-MS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adsorbent Dosage (g/L)</th>
<th>Temperature (°C)</th>
<th>Time (Minutes)</th>
<th>Cu Concentration (ppm)</th>
<th>% Cu Recovered in PLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.2</td>
<td>3M</td>
<td>180</td>
<td>4.3295</td>
<td>8.17</td>
</tr>
<tr>
<td>A2</td>
<td>0.2</td>
<td>2M</td>
<td>180</td>
<td>2.1412</td>
<td>4.04</td>
</tr>
<tr>
<td>A3</td>
<td>0.2</td>
<td>1.5M</td>
<td>180</td>
<td>13.4524</td>
<td>25.38</td>
</tr>
<tr>
<td>A4</td>
<td>0.2</td>
<td>1M</td>
<td>180</td>
<td>4.8798</td>
<td>9.21</td>
</tr>
<tr>
<td>A5</td>
<td>0.2</td>
<td>0.5M</td>
<td>180</td>
<td>1.1748</td>
<td>2.22</td>
</tr>
<tr>
<td>A6</td>
<td>0.1</td>
<td>1.5M</td>
<td>180</td>
<td>0.6935</td>
<td>1.31</td>
</tr>
<tr>
<td>A7</td>
<td>0.4</td>
<td>1.5M</td>
<td>180</td>
<td>2.1133</td>
<td>3.99</td>
</tr>
<tr>
<td>A8</td>
<td>0.6</td>
<td>1.5M</td>
<td>180</td>
<td>8.7159</td>
<td>16.45</td>
</tr>
<tr>
<td>A9</td>
<td>0.8</td>
<td>1.5M</td>
<td>180</td>
<td>10.4029</td>
<td>19.63</td>
</tr>
<tr>
<td>B1</td>
<td>0.2</td>
<td>3M</td>
<td>180</td>
<td>0.0307</td>
<td>0.06</td>
</tr>
<tr>
<td>B2</td>
<td>0.2</td>
<td>2M</td>
<td>180</td>
<td>0.0174</td>
<td>0.03</td>
</tr>
<tr>
<td>B3</td>
<td>0.2</td>
<td>1.5M</td>
<td>180</td>
<td>0.0331</td>
<td>0.06</td>
</tr>
<tr>
<td>B4</td>
<td>0.2</td>
<td>1M</td>
<td>180</td>
<td>41.2936</td>
<td>77.91</td>
</tr>
<tr>
<td>B5</td>
<td>0.2</td>
<td>0.5M</td>
<td>180</td>
<td>3.5608</td>
<td>6.72</td>
</tr>
<tr>
<td>B6</td>
<td>0.1</td>
<td>1.5M</td>
<td>180</td>
<td>11.7041</td>
<td>22.08</td>
</tr>
<tr>
<td>B7</td>
<td>0.4</td>
<td>1.5M</td>
<td>180</td>
<td>7.0196</td>
<td>13.24</td>
</tr>
<tr>
<td>B8</td>
<td>0.6</td>
<td>1.5M</td>
<td>180</td>
<td>12.3138</td>
<td>23.23</td>
</tr>
<tr>
<td>B9</td>
<td>0.8</td>
<td>1.5M</td>
<td>180</td>
<td>22.4364</td>
<td>42.33</td>
</tr>
</tbody>
</table>

The copper dissolution and percentage copper recovered at varying temperature while using Lanthanum (III) OH Adsorbent and Cerium (IV) Oxide Adsorbents are shown in Table 4-7.
4.2.6. Effect of Molar Concentration on Copper Dissolution

The variations of molar concentration of sulphuric acid was plotted against the copper dissolution in the pregnant leached solution as displayed in Figure 4-8.

![Figure 4-8: Plot of Sulphuric Acid Molar Concentration (M) against Copper Dissolution (ppm)](image)

The molar concentration of sulphuric acid has a large effect on the efficiency of the leaching process. [169] reported the low recovery of copper as a result of low concentration of acid while a high quantity of sulphuric acid will be consumed with high concentration of sulphuric acid. Also, [58] identified a direct relationship between copper recovery and acid concentration. In this investigation of copper recovery, when Lanthanum impregnated adsorbent was applied, copper dissolution rate increased until 1.5 mol/L to yield 13.45 ppm copper. The dissolution rate of copper dropped to 2.14 ppm at 2 mol/L before rising to 4.33 ppm at 3 mol/L. In a similar manner, the acid consumption and copper recovery were high till 1 mol/L concentration of sulphuric acid when Cerium impregnated adsorbents were added. The copper dissolution at 1 mol/L concentration was 41.29 ppm which is 77.91% copper recovery. The copper dissolution decreased when lixiviant concentration higher than 1 mol/L concentration of sulphuric acid lixiviant was used. When 1.5 mol/L, 2 mol/L and 3 mol/L sulphuric acid lixiviants were used, copper dissolution rate ranges between 0.03 to 0.06%. The downward trend in the recovery of copper after the 1 mol/L sulphuric acid concentration can be associated with the acid consumption by the gangue minerals [58]. The result obtained follows the trend recorded by [58] in which acid consumption and copper dissolution increased until 1.02 mol/L before decreasing thereafter. In general, the copper
dissolution rate obtained when Cerium impregnated adsorbent was added gave better copper recovery than when Lanthanum impregnated adsorbent was applied. The justification for the low recovery of copper from the solution as seen in figure 4-8 cannot be farfetched from the activation of active binding sites by the Cerium and Lanthanum impregnated adsorbents which might have attracted some copper ions thereby decreasing the copper recovery rate [160].

4.2.7. Effect of Adsorbents Dosage on Copper Dissolution

The adsorbents dosage - Lanthanum hydroxide and Cerium oxide adsorbents were plotted against the values of copper dissolution in the pregnant leached solution as presented in Figure 4-9.

![Figure 4-9: Plot of Adsorbents Dosage (g/L) against Copper Dissolution (ppm)](image)

The effect of adsorbent dosage was investigated as shown in figure 4-9, the dissolution rate of copper at different adsorbent dose differs. With the addition of Lanthanum impregnated adsorbent, copper recovery was highest at 0.2g/L dose with 13.45ppm copper recovered. At 0.1g/L dose of Lanthanum impregnated adsorbent, a low copper recovery of 0.69ppm was obtained. Copper recovery dropped to 2.11ppm at 0.4g/L before a gradual increase to 8.72ppm at 0.6g/L and then 10.4ppm at 0.8g/L. The dose of adsorbent determines the quantity of ions available willing to bond with the ions present in the process. Increased adsorbents dosage brings about an increase in the surface area willing to bond with a constant amount of ions at increased binding sites [170]. However, many factors could be responsible for the disparity in the trend of the recovery of copper in this case, coexisting ions is a major one. When Cerium impregnated adsorbent was added, the
copper recovery 11.7ppm at 0.1g/L, this is much higher than the 0.69 recovered at the same dosage of Lanthanum adsorbent. The difference can be associated with the way individual adsorbent relate with the coexisting ions in the process. The La\(^{3+}\) ions were able to engage lesser coexisting ions than the Ce\(^{3+}\) which allowed the active Cerium ions to bind with lower quantity of copper thereby resulting to higher dissolution of copper as obtained from the pregnant leached solution. This was also the case at 0.4g/L, 0.6g/L and 0.8g/L doses of Cerium adsorbent where 7.02ppm, 12.31ppm and 22.44ppm copper were recovered respectively as against the 2.11ppm, 8.72ppm and 10.4ppm obtained from the addition of Lanthanum adsorbent. However, the case was reversed at 0.2g/L dose of Cerium adsorbent in which 0.03ppm copper was recovered as against the 13.45ppm - at the same dose - obtained from the addition of Lanthanum adsorbent. The difference in the recovery rate with respect to the adsorbent dosage is the equal reaction time of 3 hours adopted for all the processes. Increasing the adsorbent dosage shortens the time required for the reaction to complete as lower dose of adsorbent will take a longer time for the adsorbents ions and other ions existing in the solution bond. However, key disadvantages of using higher dosage of adsorbent are increase in cost and increase in chemical consumption [171].

4.2.8. Effect of Temperature on Copper Dissolution

The temperature variations were plotted against the values of copper dissolution in the pregnant leached solution as presented in Figure 4-10.

![Figure 4-10: Plot of Temperature (°C) against Copper Recovery (ppm)](image)

Figure 4-10: Plot of Temperature (°C) against Copper Recovery (ppm)
The result displayed in figure 4-10 shows 25.38% at 25°C maximum copper recovery and 0.09% minimum at 65°C and 80°C with the application of Lanthanum adsorbent while the application of Cerium adsorbent yielded a maximum recovery of 19.27% at 80°C and 0.06% minimum Cu dissolution at 25°C.

The application of Cerium adsorbent align with conventional findings in which increase in temperature brings about increase in copper recovery [58], [172]. With the application of Cerium adsorbent, higher temperature clearly increased the dissolution of copper. Carlesi et al [173] related this to the physicochemical properties which has effects on the transport phenomena. The addition of Lanthanum adsorbent however gave a strange dissolution trend as increase in temperature yielded a decrease in copper recovery. This cannot be divulged from the intrinsic chemical reactions introduced by the addition of La$^{3+}$ ions; this generally affects the linear behavior with temperature variation [173].

4.2.9. Chemical Analysis of Iron in Pregnant Leach Solution

Table 4-8 present the Iron dissolution and percentage iron removed at varying parameters such as Lanthanum (III) OH Adsorbent Dosage, Cerium (IV) Oxide Adsorbent Dosage and Molar Concentration of sulphuric acid lixiviant. Furthermore, table 4-9 display the iron dissolution and percentage iron removed at varying temperature and using Lanthanum (III) OH Adsorbent and Cerium (IV) Oxide Adsorbents.

Table 4-8: Iron Dissolution and % Removal after final characterization using ICP-MS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adsorbent Dosage (g/L)</th>
<th>Molar Concentration</th>
<th>Time (minutes)</th>
<th>Iron Concentration (ppm)</th>
<th>% Fe Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.2</td>
<td>3M</td>
<td>180</td>
<td>36.1103</td>
<td>99.84</td>
</tr>
<tr>
<td>A2</td>
<td>0.2</td>
<td>2M</td>
<td>180</td>
<td>32.1460</td>
<td>99.86</td>
</tr>
<tr>
<td>A3</td>
<td>0.2</td>
<td>1.5M</td>
<td>180</td>
<td>25.7541</td>
<td>99.89</td>
</tr>
<tr>
<td>A4</td>
<td>0.2</td>
<td>1M</td>
<td>180</td>
<td>15.1793</td>
<td>99.93</td>
</tr>
<tr>
<td>A5</td>
<td>0.2</td>
<td>0.5M</td>
<td>180</td>
<td>6.3048</td>
<td>99.97</td>
</tr>
<tr>
<td>A6</td>
<td>0.1</td>
<td>1.5M</td>
<td>180</td>
<td>23.3592</td>
<td>99.90</td>
</tr>
<tr>
<td>A7</td>
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<td>1.5M</td>
<td>180</td>
<td>29.9352</td>
<td>99.87</td>
</tr>
<tr>
<td>A8</td>
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<td>1.5M</td>
<td>180</td>
<td>19.6417</td>
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</tr>
<tr>
<td>A9</td>
<td>0.8</td>
<td>1.5M</td>
<td>180</td>
<td>19.3298</td>
<td>99.91</td>
</tr>
</tbody>
</table>
Table 4-9: Iron Dissolution and % Removal obtained at varying temperature using 1.5M sulphuric acid lixiviant after final characterization using ICP-MS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adsorbent</th>
<th>Adsorbent Dosage (g/L)</th>
<th>Temperature (°C)</th>
<th>Time (Minutes)</th>
<th>Fe Concentration (ppm)</th>
<th>% Fe Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>La (III) OH</td>
<td>0.2</td>
<td>25</td>
<td>180</td>
<td>25.7541</td>
<td>99.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2</td>
<td>40</td>
<td>180</td>
<td>42.7964</td>
<td>99.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2</td>
<td>50</td>
<td>180</td>
<td>48.3276</td>
<td>99.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2</td>
<td>65</td>
<td>180</td>
<td>39.0352</td>
<td>99.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2</td>
<td>80</td>
<td>180</td>
<td>37.1106</td>
<td>99.84</td>
</tr>
<tr>
<td></td>
<td>Ce (IV) OH</td>
<td>0.2</td>
<td>25</td>
<td>180</td>
<td>29.4246</td>
<td>99.87</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>180</td>
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<tr>
<td></td>
<td></td>
<td>0.2</td>
<td>80</td>
<td>180</td>
<td>50.3494</td>
<td>99.78</td>
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</table>

4.2.10. Effect of Molar Concentration on Iron Dissolution

The variations of molar concentration of sulphuric acid were plotted against the % iron removal in the ore as displayed in Figure 4-11. adsorbents dosage – Lanthanum hydroxide and Cerium oxide – and temperature were plotted against the % iron removal in the ore as displayed in Figures 4-11 and 4-12 respectively.
As shown in Figure 4-11, the dissolution of iron in the experiment decreases with increasing acid molarity with the addition of Lanthanum nanoparticles adsorbents. At 0.5M of sulphuric acid, 99.97% of iron was dissolved, however, at 3M of sulphuric acid, 99.84% Fe was dissolved. The anomalous behavior of this dissolution-molarity relation can be assumed to be as a result of the addition of the Lanthanum adsorbent. This is due to the polymerization of the Lanthanum adsorbents at increased molarity of sulphuric acid. This is a deviation from the results obtained from literature. [174] reported an increasing iron dissolution percentage with increasing sulphuric acid molarity. However, with the addition of Cerium nanoparticles adsorbents, the dissolution percentage of iron has no uniform trend. At 0.5M of sulphuric acid, it can be observed that 99.85% Fe was dissolved while the highest dissolution was observed at 1M of sulphuric acid in which 99.92% Fe was dissolved. It can be conceded that the effect of the adsorbent on the environment determines the dissolution behavior of iron.

4.2.11. Effect of Adsorbents Dosage on Iron Dissolution

The variations of adsorbents dosage – Lanthanum hydroxide and Cerium oxide were plotted against the % iron removal in the ore as shown in Figure 4-12.
The effect of adsorbent dosage on iron dissolution as observed in figure 4-12 shows an interference of competing ions. The behavior of other ions with the addition of Lanthanum and Cerium nanoparticles adsorbents has a huge effect on the dissolution of iron and copper in the experiment. With the addition of Lanthanum and Cerium nanoparticles adsorbents, the dissolution percentage of iron ranges from 99.81% to 99.97%. This shows a high dissolution of iron which is in conformity with those reported in literature [58], [59], [172].

4.2.12. Effects of Co-Existing Constituents

The characterization of the residues gotten from varying the molar concentration of sulphuric acid from 3M, 2M, 1.5M, 1M and 0.5M as represented by A1, A2, A3, A4 and A5 respectively for Lanthanum nanoparticles adsorbents and B1, B2, B3, B4 and B5 for Cerium nanoparticles adsorbents gave the results presented in Tables 4-10 and 4-11.

Also, the characterization of the residue obtained from the variation of adsorbents dosage from 0.1g/L, 0.4 g/L, 0.6 g/L and 0.8 g/L as represented by A6, A7, A8 and A9 for Lanthanum nanoparticles adsorbent and B6, B7, B8 and B9 for Cerium nanoparticles adsorbents gave the result displayed in Table 4-12; and the result obtained from the characterization of the residue obtained from the variation of the temperature from 25°C, 40°C, 50°C, 65°C and 80°C as represented by T1, T2, T3, T4 and T5 for Lanthanum nanoparticles adsorbents and T6, T7, T8, T9 and T10 for Cerium nanoparticles adsorbents gave the results shown in Table 4-13.
Table 4-10 presents the other elements and ions retained in the residue of the process when sulphuric acid lixiviant with varying molar concentration and 0.2 g/L Lanthanum hydroxide adsorbent were used at room temperature.
Table 4-10: Elemental Analysis of Residue of Samples A1, A2, A3, A4 and A5

<table>
<thead>
<tr>
<th>Components</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>2.97</td>
<td>0.05</td>
<td>0.04</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Mg</td>
<td>0.28</td>
<td>0.42</td>
<td>0.58</td>
<td>1.15</td>
<td>1.17</td>
</tr>
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Table 4-11 shows the other elements and ions retained in the residue of the process when sulphuric acid lixiviant with varying molar concentration and 0.2g/L Cerium hydroxide adsorbent were used at room temperature.
Table 4-11: Elemental Analysis of Residues of B1, B2, B3, B4 and B5

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<td>12.08</td>
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Table 4-12 shows the other elements and ions retained in the residue of the leaching and adsorption process when sulphuric acid lixiviant with 1.5 molar concentration and different adsorbents dosage were used at room temperature.
Table 4-12: Elemental Analysis of Residues of A6, A7, A8, A9, B6, B7, B8 and B9.

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Table 4-13 shows the other elements and ions retained in the residue of the leaching and adsorption process when sulphuric acid lixiviant with 1.5 molar concentration and 0.2g/L adsorbents dosage were used at varying temperature.
Table 4-13: Elemental Analysis of Residues of T1, T2, T3, T4, T5, T6, T7, T8, T9 and T10.

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<td>Zr</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.05</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Nb</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>1.8</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Ba</td>
<td>0.2</td>
<td>0.36</td>
<td>0.4</td>
<td>0.43</td>
<td>NA</td>
<td>0.61</td>
<td>0.44</td>
<td>0.34</td>
<td>0.31</td>
<td>0.23</td>
</tr>
</tbody>
</table>

As observed in Tables 4-10, 4-11, 4-12 and 4-13, the effect of different competing ions is obvious from the adsorption amount obtained at various parameters studied. At room temperature, higher quantity of SO$_3$ ions interacted with the adsorbents than the quantity that interacted with the adsorbent at elevated temperature. More SO$_3$ ions were dissolved at elevated temperature than at room temperature. This compares with [175] experiment in which SO$_3$ influenced the adsorption
of arsenic by decreasing the adsorption capacity with elevated temperature. The higher interaction of SO$_3$ with the adsorbents at room temperature will consequentially reduce the surface interaction of arsenic and the nanoparticles adsorbents, which limits the potential of the adsorbents. This is as a result of competition between the sulphur ions and arsenic to fill in the active sites of the adsorbents. SO$_3$ has stronger affinity for rare earth adsorbents than As(III) and As(V). This stronger affinity decreases the removal efficiency of arsenic on Lanthanum and Cerium nanoparticles adsorbent. Similarly, Ca$^{2+}$ greatly influenced the interaction between the adsorbents and arsenic due to its high quantity in the ore sample. The Ca$^{2+}$ ions did not dissolve in the sulphuric acid solution, it instead was retained in the leachate thereby competing with arsenic for the active sites in the adsorbents. The huge concentration of Ca$^{2+}$ has a competitive advantage in the process and will consequentially reduce the adsorption ability of the adsorbents. Other notable ions include Mg$^{2+}$, Al$^{3+}$, SiO$_2$, K$^+$, Ti$^{2+}$ and Ba$^{2+}$. Meanwhile, Al$^{3+}$, K$^+$, Ti$^{2+}$ and Ba$^{2+}$ at room temperature and elevated temperature reacted in a similar manner as SO$_3$ and Ca$^{2+}$ but with lesser effects due to their lower concentration. There is more competition between these ions and As(III) than with As(V) at elevated temperature due to their infinity for the adsorbent’s active sites. However, Mg$^{2+}$ and SiO$_2$ had a different reaction behaviour at elevated temperature. Their dissolution rate in sulphuric acid increases with increasing temperature thereby depicting more active interaction with adsorbents and competition with arsenic ions for active sites at room temperature [16], [165], [176].

4.3. ARSENIC ADSORPTION

The variation in the adsorption of arsenic on the sorbents is plotted against the samples. Figure 4-13 shows the % adsorption at different variation of molar concentration and Lanthanum nanoparticles dosage.
As observed in Figure 4-13, the %As adsorption on Lanthanum nanoparticles adsorbent is lower at higher sulphuric acid molarity and higher at lower sulphuric acid molarity. This can be explained by activities of movements of ions in the system. At higher concentration of acid, there is a significant level of excitation of ions in the system which thereby reduces the likelihood of possible interaction between the arsenic molecules and Lanthanum nanoparticles adsorbents. Sulphuric acid reacts better with the arsenic ions due to the quantity as against the limited quantity of Lanthanum ions and the possibility of binding with the ions introduced by the acid. This causes a greater excitation of As(III) than with As(V), this consequentially creates a kind of imbalance in the system as the two particles meet each other. This kind of decrease in the difference between the adsorbent and the arsenic ions excitation state causes both ions to ricochet off one another when they come in contact. However, adsorbent of arsenic was higher at increased dosage of Lanthanum nanoparticles adsorbents, this shows an increase in the number of Lanthanum ions present in the system thereby increasing the active cells. The increase in the activities of the adsorbents ions consequentially increases the rate of binding with As(III) than with As(V) which explains the reason for an increased adsorption [166], [167], [177], [177].

The % adsorption at different variation of molar concentration and Cerium nanoparticles dosage is displayed in Figure 4-14.
In the case of Cerium adsorbent, there is a deviation. The Cerium ions were able to actively react with arsenic at higher acid molarity, hence, causing higher adsorption at higher molarity of acid than lower molar mass. However, with the increase in Cerium nanoparticles adsorbent dosage, the interaction between adsorbents and arsenic ions reduces. This can be assumed to be as a result of the lack of equal activeness and composition of the two ions which affected the equilibrium of the system [178], [179].

In Figure 4-15, the % adsorption at similar adsorbent dosages and molar concentrations in samples where Lanthanum nanoparticles adsorbent is used and samples where Cerium nanoparticles adsorbent is used are compared for clear display of disparity in % adsorption.
Compared to other parameters studied for Lanthanum nanoparticles adsorbents, the adsorption of arsenic was higher at elevated temperature, depicting an equilibrium state of the system whereby both ions were active, and this makes it possible for bonding to occur easily. The stronger the interaction between the two ions, the more active the ions are and the more the adsorption that occurs. Meanwhile, the activity of Cerium ions increased with increasing temperature until the system was no longer at the state of equilibrium, this explains the reason for lower adsorption at higher temperature [164]–[167].

4.4. **ADSORPTION MODEL**

The adsorption data for the addition of Lanthanum nanoparticles adsorbent is given in Table 4-15.
The adsorption data for Cerium nanoparticles adsorbent is given in Table 4-16.

Table 4-16: Adsorption Data for Cerium Nanoparticles Adsorbent

<table>
<thead>
<tr>
<th>Samples</th>
<th>C₀ (%wt)</th>
<th>Cₑ (%wt)</th>
<th>V (L)</th>
<th>m (g)</th>
<th>qₑ (g/L)</th>
<th>% Adsorption</th>
<th>Parameters (H₂SO₄ Molarity and Adsorbent Dosage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.0024</td>
<td>0.00031987</td>
<td>0.1</td>
<td>0.2</td>
<td>0.001040065</td>
<td>86.67208333</td>
<td>3M H₂SO₄ and 0.2g/L</td>
</tr>
<tr>
<td>A2</td>
<td>0.0024</td>
<td>0.00038197</td>
<td>0.1</td>
<td>0.2</td>
<td>0.001009015</td>
<td>84.08458333</td>
<td>2M H₂SO₄ and 0.2g/L</td>
</tr>
<tr>
<td>A3</td>
<td>0.0024</td>
<td>0.00018216</td>
<td>0.1</td>
<td>0.2</td>
<td>0.00110892</td>
<td>92.41</td>
<td>1.5M H₂SO₄ and 0.2g/L</td>
</tr>
<tr>
<td>A4</td>
<td>0.0024</td>
<td>0.00000338</td>
<td>0.1</td>
<td>0.2</td>
<td>0.00119831</td>
<td>99.85916667</td>
<td>1M H₂SO₄ and 0.2g/L</td>
</tr>
<tr>
<td>A5</td>
<td>0.0024</td>
<td>0.00002516</td>
<td>0.1</td>
<td>0.2</td>
<td>0.00118742</td>
<td>98.95166667</td>
<td>0.5M H₂SO₄ and 0.2g/L</td>
</tr>
<tr>
<td>A6</td>
<td>0.0024</td>
<td>0.00006629</td>
<td>0.1</td>
<td>0.2</td>
<td>0.001166855</td>
<td>97.23791667</td>
<td>1.5M H₂SO₄ and 0.1g/L</td>
</tr>
<tr>
<td>A7</td>
<td>0.0024</td>
<td>0.00018821</td>
<td>0.1</td>
<td>0.2</td>
<td>0.001105895</td>
<td>92.15791667</td>
<td>1.5M H₂SO₄ and 0.4g/L</td>
</tr>
<tr>
<td>A8</td>
<td>0.0024</td>
<td>0.00001127</td>
<td>0.1</td>
<td>0.2</td>
<td>0.001194365</td>
<td>99.53041667</td>
<td>1.5M H₂SO₄ and 0.6g/L</td>
</tr>
<tr>
<td>A9</td>
<td>0.0024</td>
<td>0.00004346</td>
<td>0.1</td>
<td>0.2</td>
<td>0.00117827</td>
<td>98.18916667</td>
<td>1.5M H₂SO₄ and 0.8g/L</td>
</tr>
</tbody>
</table>

The adsorption data for Lanthanum nanoparticles adsorbent is given in Table 4-16.
The parameters of adsorption of arsenic on Lanthanum nanoparticles and Cerium nanoparticles adsorbents are given in Tables 4-15 and 4-16 respectively. With the application of Lanthanum nanoparticles adsorbent, the values of $R^2$ obtained as calculated from Table 4-15 for all the variation carried out are 1. The values of $R_L$ obtained for each of the adsorption carried out using Lanthanum nanoparticles are greater than 1. This shows that the adsorption nature is unfavourable for Lanthanum nanoparticles adsorbent [180].

With the application of Cerium nanoparticles adsorbent, the $R^2$ values obtained as calculated from Figure 4-16 for all the variation carried out are 1. Meanwhile, the values of $R_L$ obtained for all the variations B1, B2, B3, B4, B5, B6, B7, B8 and B9 as derived from Table 4-16 is unity. This shows a linear adsorption nature. The application of Cerium nanoparticle adsorbent fits into the Langmuir adsorption isotherm model and shows the feasibility of applying Cerium nanoparticles adsorbent over the Lanthanum nanoparticles adsorbent. As observed, the Lanthanum nanoparticles adsorbent performance dropped with increasing acid molarity while the performance of Cerium nanoparticle adsorbent increases with increasing molarity. This is obvious from the adsorption quantity calculated in Tables 4-15 and 4-16. At 3M of sulphuric acid and 0.2g/L adsorbent dosage, Lanthanum nanoparticle adsorbent adsorbed 86.67% As while Cerium nanoparticle adsorbent adsorbed 99.94%As; at 2M of sulphuric acid and 0.2g/L adsorbent dosage, Lanthanum nanoparticle adsorbent adsorbed 84.08% As while Cerium nanoparticle adsorbent adsorbed 99.99%As; at 1.5M of sulphuric acid and 0.2g/L adsorbent dosage, Lanthanum nanoparticle adsorbent adsorbed 92.41% As while Cerium nanoparticle adsorbent adsorbed 98.56%As; at 1M of sulphuric acid and 0.2g/L adsorbent dosage, Lanthanum nanoparticle adsorbent adsorbed 99.85% As while Cerium nanoparticle adsorbent adsorbed 90.66%As; at 0.5M of sulphuric acid and 0.2g/L adsorbent dosage, Lanthanum nanoparticle adsorbent adsorbed 98.95% As while Cerium nanoparticle adsorbent adsorbed 97.14%As. However, Lanthanum nanoparticle adsorbent performed better with increasing dosage at 1.5M concentration of acid than Cerium nanoparticle adsorbent. At 0.1g/L of each, Lanthanum nanoparticle adsorbent adsorbed 97.24% As while Cerium nanoparticle adsorbent adsorbed 93.55% As, at 0.4g/L of each, Lanthanum nanoparticle adsorbent adsorbed 92.15% As while Cerium nanoparticle adsorbent adsorbed 96.54% As, at 0.6g/L of each, Lanthanum nanoparticle adsorbent adsorbed 99.53% As while Cerium nanoparticle adsorbent adsorbed 86.69% As, and at 0.8g/L of each, Lanthanum nanoparticle adsorbent adsorbed 98.19% As while Cerium nanoparticle adsorbent adsorbed 84.33% As.
CHAPTER 5: CONCLUSION

This research encompasses the characterization of a low-grade copper oxide ore using atomic absorption spectrometer, x-ray fluorescence (XRF), x-ray diffractometer (XRD), SEM-EDS and Induced Coupled Plasma Mass Spectroscopy (ICP-MS); leaching and adsorption of the copper ore sample was carried out using sulphuric acid of varying molarity -3M, 2M, 1.5M, 1M and 0.5M – and two Lanthanum and Cerium nanoparticles adsorbents were prepared for the adsorption of arsenic from the ore sample during the hydrometallurgical extraction of copper -leaching- process.

The findings are as follows: First, the atomic absorption spectroscopy revealed a copper concentration of 53.2ppm, arsenic concentration of 24.4ppm and iron concentration of 22335ppm which is not far from accuracy when compared with the result obtained from the characterization carried out using XRF in which 53ppm, 24ppm and 22 3574 ppm of copper, arsenic and iron respectively were reported.

Second, quartz, quicklime (CaO), larnite (Ca₂SiO₄), hatrurite, magnetite, dolomite, calcite, wustite, hongquite, nichromite, franklinite and spine were found to be the gangue minerals present in the ore. Calcite occurrence was found to be evident and high in concentration while the very low content of arsenic and copper made it impossible for the x-ray diffraction method to detect their presence. Also, the SEM-EDS could not detect the copper and arsenic phases due to the low-grade value of the ore. However, the particle of the associated minerals has an average particle size of 400nm in diameter. This was given by an irregular surface dominated by calcite. From the micrograph, it was discovered that the materials present in the sample are aggregated partially. Elements reported by the EDS include magnesium, aluminium, silica, sulphur, potassium, manganese, calcium, titanium and iron.

Third, there is a direct relationship between the concentration of acid and arsenic dissolution. The %As adsorption on Lanthanum nanoparticles adsorbent is lower at higher acid molarity and higher at lower sulphuric acid molarity. While in the case of Cerium adsorbent, there is a deviation. The Cerium ions were able to actively react with arsenic at higher acid molarity hence causing higher adsorption at higher molarity of acid than lower molar mass. It was also found that arsenate removal efficiency increases sharply with increasing adsorbent dosage, though there were some anomalies which were observed to be because of competing ions on the adsorption. In addition,
increase in temperature was found to reduce the adsorption efficiency of the both the Cerium and Lanthanum nanoparticles adsorbents.

The effect of acid molarity, adsorbent dosage and temperature were also studied on copper and iron dissolution in the extraction process. Low copper dissolution rate was achieved due to the activation of active binding sites by the Cerium and Lanthanum adsorbents which might have attracted some copper ions. The copper dissolution rate obtained when Cerium impregnated adsorbent was used gave better copper recovery than when Lanthanum adsorbents were applied.

The values of $R_L$ obtained for each of the adsorption carried out shows that the nature of Langmuir model is unfavourable for Lanthanum nanoparticles, but the linear value obtained for $R_L$ in the case of Cerium nanoparticles makes it fit into the model. It is important to note that Cerium nanoparticles adsorbent performs better with increasing acid molarity while Lanthanum nanoparticles adsorbent performs better with increasing adsorbent dosage.

Further research can be carried out to explore the performance of these adsorbents in other efficient copper leaching lixiviants such as alkaline glycine and ammonia. The reusability of the adsorbent should also be studied for the sake of understanding the economic viability of the process. A more elaborate study could be conducted by considering a molecular dynamics simulation of these molecular interactions which could thereafter be compared to the obtained elemental values to predict a more accurate model for application in the industry.
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### APPENDIX 1

Table A: Adsorption Quantity when Cerium Nanoparticle Adsorbent is applied

<table>
<thead>
<tr>
<th>Samples</th>
<th>( C_0 ) (%wt)</th>
<th>( C_e ) (%wt)</th>
<th>V (L)</th>
<th>m (g)</th>
<th>( q_e ) (g/L)</th>
<th>% Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.0024</td>
<td>0.00031987</td>
<td>0.1</td>
<td>0.2</td>
<td>0.001040065</td>
<td>86.67</td>
</tr>
<tr>
<td>A2</td>
<td>0.0024</td>
<td>0.00038197</td>
<td>0.1</td>
<td>0.2</td>
<td>0.001009015</td>
<td>84.09</td>
</tr>
<tr>
<td>A3</td>
<td>0.0024</td>
<td>0.00018216</td>
<td>0.1</td>
<td>0.2</td>
<td>0.00110892</td>
<td>92.41</td>
</tr>
<tr>
<td>A4</td>
<td>0.0024</td>
<td>0.00000338</td>
<td>0.1</td>
<td>0.2</td>
<td>0.00119831</td>
<td>99.86</td>
</tr>
<tr>
<td>A5</td>
<td>0.0024</td>
<td>0.00002516</td>
<td>0.1</td>
<td>0.2</td>
<td>0.00118742</td>
<td>98.95</td>
</tr>
<tr>
<td>A6</td>
<td>0.0024</td>
<td>0.00006629</td>
<td>0.1</td>
<td>0.2</td>
<td>0.001166855</td>
<td>97.24</td>
</tr>
<tr>
<td>A7</td>
<td>0.0024</td>
<td>0.00018821</td>
<td>0.1</td>
<td>0.2</td>
<td>0.001105895</td>
<td>92.16</td>
</tr>
<tr>
<td>A8</td>
<td>0.0024</td>
<td>0.0001127</td>
<td>0.1</td>
<td>0.2</td>
<td>0.001194365</td>
<td>99.53</td>
</tr>
<tr>
<td>A9</td>
<td>0.0024</td>
<td>0.0004346</td>
<td>0.1</td>
<td>0.2</td>
<td>0.00117827</td>
<td>98.19</td>
</tr>
</tbody>
</table>

Table B: Adsorption Quantity when Cerium Nanoparticle Adsorbent is applied

<table>
<thead>
<tr>
<th>Samples</th>
<th>( C_0 ) (%wt)</th>
<th>( C_e ) (%wt)</th>
<th>V (L)</th>
<th>m (g)</th>
<th>( q_e ) (g/L)</th>
<th>% Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>0.0024</td>
<td>0.0001117</td>
<td>0.1</td>
<td>0.2</td>
<td>0.001194415</td>
<td>99.54</td>
</tr>
<tr>
<td>B2</td>
<td>0.0024</td>
<td>0.000000026</td>
<td>0.1</td>
<td>0.2</td>
<td>0.0011987</td>
<td>99.99</td>
</tr>
<tr>
<td>B3</td>
<td>0.0024</td>
<td>0.00003448</td>
<td>0.1</td>
<td>0.2</td>
<td>0.00118276</td>
<td>98.56</td>
</tr>
<tr>
<td>B4</td>
<td>0.0024</td>
<td>0.00022412</td>
<td>0.1</td>
<td>0.2</td>
<td>0.00108794</td>
<td>90.66</td>
</tr>
<tr>
<td>B5</td>
<td>0.0024</td>
<td>0.00006855</td>
<td>0.1</td>
<td>0.2</td>
<td>0.001165725</td>
<td>97.14</td>
</tr>
<tr>
<td>B6</td>
<td>0.0024</td>
<td>0.00015471</td>
<td>0.1</td>
<td>0.2</td>
<td>0.001122645</td>
<td>93.55</td>
</tr>
<tr>
<td>B7</td>
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<td>0.0000829</td>
<td>0.1</td>
<td>0.2</td>
<td>0.00115855</td>
<td>96.55</td>
</tr>
<tr>
<td>B8</td>
<td>0.0024</td>
<td>0.00031938</td>
<td>0.1</td>
<td>0.2</td>
<td>0.00104031</td>
<td>86.69</td>
</tr>
<tr>
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<td>0.0024</td>
<td>0.00037598</td>
<td>0.1</td>
<td>0.2</td>
<td>0.00101201</td>
<td>84.33</td>
</tr>
</tbody>
</table>
APPENDIX 2

Plate 1: Filtering After Agitation
Plate 2: Samples and Filtering
Plate 3: Filtering
APPENDIX 5

Plate 4: Filtering
APPENDIX 6

Plate 5: Adsorption Experiment
Plate 6: Presentation of Research at TMREES-18 Conference, Athens, Greece