SOLVENT EXTRACTION OF ZINC FROM BURNT TYRE ASH USING TRI BUTYL PHOSPHATE

Abstract

The extraction of metals for economic value after acid/alkaline leaching is key to their utilization industrially. This study reported the Solvent extraction using Tributylphosphate (TBP) for obtaining zinc from burnt tyre ash leach liquor after leaching in hydrochloric acid (HCl). As a result, this study aims to leach out zinc from the secondary sources (burning tyre ash) using HCl at the predetermined optimal condition and determining the HCl concentration, leaching time, temperature and agitation speed and to determine the concentration of zinc in the leached liquor using atomic absorption spectrophotometry, this can help address the resource recovery, offering potential environmental, economic, technological benefits of Zinc and dual challenges of waste management.

Methodology:

Burnt tyre ash of (2.5 g) was dissolved in a 250 cm^3 prepared solution of HCl and introduced on a heating magnetic stirrer at 68.85°C at an ambient temperature of 25°C for less than 2 hours and the zinc concentration was measured by Atomic Absorption Spectrophotometry after filtration and dilution. The filtrate was then carefully transferred into a 250ml standard volumetric flask and made to mark with distilled water, the filtrate in the standard volumetric flask was then adjusted to pH 3.5 and analysis was carried out using Atomic Absorption Spectroscopy at a room temperature of 25±2°C. A TBP concentration of 0.05M, 0.10M, 0.15M, 0.20M, 0.25M and 0.30M were used, 10 cm^3 of each concentration of the extractant (TBP)

with 10 cm^3 of the leachate from the AAS were mixed in a 250 cm^3 conical flask and shaked for 25 minutes at room temperature at a pH 4.5 and it was allowed to form two separation layers. The upper one contained Zn loaded organic phase while the lower part had a clear solution. The concentration of Zn in each experimental group of TBP concentration was calculated.

Results:

The results of solvent extraction of zinc by 0.30 mol/L TBP in kerosene yielded 35.05 % extraction efficiency within 25 minutes at 25 ± 2ºC. At optimal conditions, the study showed that a phase ratio of 1:1 for the organic : aqueous phase extracted 48.68 % of the total zinc into the organic phase at pH 4.5, of which 60% of the loaded organic phase was quantitatively stripped by 0.05mol/L HCl solution.

Conclusion:

Based on the findings in this study, it was concluded that TBP is an effective solvent for the extraction of zinc from waste especially burnt tyre ash leach liquor under the specified conditions and can serve as raw materials for industrial products.

Keywords*: *Zinc, Burnt tyre ash, leashing, Tributylphosphate (TBP), extraction.

INTRODUCTION

With the growing interest in environmental protection in recent years, the problem of tyre waste disposal has been closing up in Japan (Chen *et al.*, 2022). Among the concerns under discussion are emissions of hazardous chemical species during the waste incineration, spontaneous combustion of the waste in storage and secondary pollution by heavy metal highly concentrated in the combustion residue. According to Japan Automobile Tyre Manufacturers Association (JATMA) in 2019, Globally millions of tonnes of tyres are produced annually, increasing year-on-year, and thereby increasing the waste stream by over one million.

The recycling system in automobile and the recycling rates of tyre waste in 2002 was reported as high as 87%, which consists of material recycling (13%), product recycling (18%) and thermal recovery (56%). In general, automobile tyres consists of rubber, carbon black, and a variety of organic and inorganic additives (including plasticizers, anti-aging agents, sulfur and zinc oxide, etc (Niezgoda et al., 2020; Malinova, 2022). Heavy metals are concentrated in combustion ashes during incineration process and the residues are now disposed as industrial waste under strict regulation. However, the resulting combustion ashes would be potential sources of these metals; whole tyre wastes annually generated an estimated of 7000 tonnes for zinc, so drawing attention to the recovery of valuable metals from waste scrap and dumpsite ashes (Xu *et al.*, 2020).

Many investigations have been conducted on the leaching behaviour and the recovery system of heavy metals from industries wastes, heavy oil ashes (Salehin *et al.*, 2016), municipal solid wastes (Krishnan *et al.*, 2021), coal ashes, waste catalyst (Wang *et al.*, 2014), sewage sludge and residue from waste water treatment plant (Demirbas et al., 2017) and spent batteries (Makuza *et al.*, 2021).

However, there has been little attention on the metal recovery from combustion ashes derived from tyre waste. The metal leaching behaviour of fly and bottom ashes should be ascertained in order to recover leached valuable metals from them, through a hydrometallurgical process.

1.1 Chemistry of Zinc

Zinc is a chemical element belonging to Group 12 (IVa) of the periodic table with the symbol Zn and atomic no 30. It is the 24th most abundant element in the earth's crust and has five stable isotopes such as 64Zn, 66Zn, 67Zn, 68Zn and 70Zn (Steller et al., 2022). The most common isotope is 64Zn with 48.63% share of the natural isotope ratio. This is followed by 66Zn with 27.90%, 68Zn with 18.75%, 67Zn with 4.10%, and the rarest natural isotope 70Zn with a share of 0.62%. It is the fourth most widely consumed metal after iron, aluminium and copper. It is a moderately reactive metal and strong reducing agent; it has low melting point and boiling point, and is silvery white. Zinc crystallizes in a hexagonal close-packed sphere. Zinc dissolves in acids to form zinc (II) salts and in alkalis to form zincates, [Zn(OH)4]2 (Kania et al., 2023).

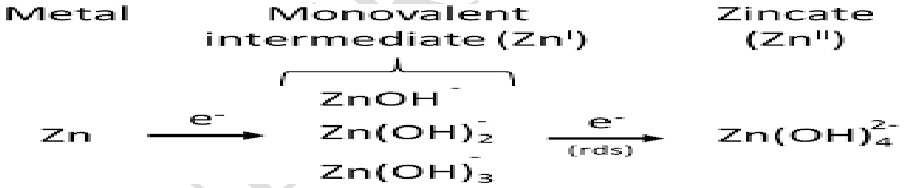

Figure 1.0: Reaction of Zinc to form Zincates

An exception is zinc with very high purity (99.999%), which does not react with acids. Zinc is in its compounds almost without exception in the oxidation state +2. The most stable artificial isotope is the beta and gamma emitter (K / β + decay) 65Zn with a half-life of 244 days. This and the core isomer 69m serve as tracers. As the only natural isotope, 67Zn can be detected by NMR spectroscopy (Xu et al., 2019). Chemically, zinc is one of the base metals (redox potential -0.763 volts).

Zinc is predominantly obtained from zinc sulphide ores. To use these, they must first be converted to zinc oxide. This is done by roasting in the air. In addition to the zinc oxide, large quantities of sulphur dioxide are formed, which can be further processed to sulphuric acid. Smithsonite is used as a raw material; this can be done by burning with elimination of carbon dioxide (Kaya et al., 2020). The further processing can be done by two possible methods. These are the wet and dry procedures. In 2015, total zinc production amounted to 13.4 million tonnes and another 14 million tonnes was recovered from recycling (Sabnavis et al., 2018).

1.2 Mineralogical Study of Zinc

The specific mineralogy of zinc ores can vary depending on the deposit's geology, geochemistry, and mineralization processes. Zinc ores are typically found in nature as various minerals. It refers to the naturally occurring rock or mineral that contains a significant concentration of zinc. Mostly zinc is bound in ores. The most common and most important for the production of zinc ores is zinc sulphide ores. These are naturally either sphalerite or wurtzite and contain about 65% zinc. Another zinc ore is Galmei, which refers to both Smithsonite (also zinc spar) ZnCO3 (about 52% zinc) and Willemite Zn2 [SiO4]. In addition, there are even rarer zinc minerals such as zincite (also red zinc ore) ZnO (about 73% zinc), hemimorphite Zn4 (OH)2 Si2O7] (54% zinc), adamine Zn2 (AsO4) (OH) (about 45% Zinc), minrecordite Ca Zn [CO3]2 (about 29% zinc) and franklinite (Zn, Fe, Mn) (Fe2Mn2) O4 (16% zinc). Altogether there are currently known about 300 zinc minerals. They occur in different types of ore deposit including sulphide deposits carbonate-hosted deposits, and oxide deposits (Leach et al., 2019)

The mining and processing of zinc ores involve various techniques, including underground or open-pit mining, followed by crushing, grinding, and flotation or other beneficiation processes to separate the zinc minerals from the gangue minerals. The resulting zinc concentrate is then further processed through smelting or electrolysis to obtain zinc metal or other zinc-containing products (Van et al., 2016). It is usually foundations in hydrothermal veins, as well as in sedimentary, metamorphic, and igneous rocks.

Sphalerite can vary in colour from yellow, brown, and black to red, green, and transparent, depending on its impurities. It has a resinous to adamantine lustre when freshly broken, but may become dull upon exposure to air. Zinc ore has a hardness of 3.5 to 4.0 on the Mohr’s scale, which means it is relatively soft and can be scratched with a knife or a fingernail (Oluwasegun et al., 2021). The density of zinc ore varies depending on its composition and impurities, but typically ranges from 3.9 to 4.2 g/cm³.

Zinc ore is primarily composed of zinc sulphide (ZnS), but it may also contain varying amounts of other elements, such as iron, cadmium, indium, and gallium, as impurities. It is relatively stable and does not react with air or water at normal temperatures. However, it can react with acids, producing hydrogen gas and soluble zinc salts. Zinc ore is typically opaque, meaning that it does not transmit light. Some zinc ores exhibit fluorescence under ultraviolet (UV) light, emitting a characteristic glow that can be used for identification purposes, Zinc ore is a poor conductor of electricity, as it is an insulating mineral, Zinc ore is not magnetic and does not exhibit any magnetic properties. Detailed mineralogical studies and analyses are typically conducted to identify and characterize the specific zinc ore minerals present in a given deposit, which can provide valuable information for exploration, mining, and processing of zinc ores (Kania et al., 2023).

1.3 Secondary Sources of Zinc

According to International Zinc Association, there are 50 secondary zinc operators in the world with varying recycling processes (Kaya et al., 2020). New scrap is usually reheated. In the case of mixed non-ferrous shredded metal scrap, zinc is separated by hand or magnetically, before it is refined by retorting. An important source of secondary zinc is flue dust from secondary electric arc furnaces for production of iron, using galvanized iron scrap. Consumption of refined zinc metal in recent years has been slightly more than total metal production, perhaps due to the considerable amount of refined zinc includes zinc used directly in alloys irrespective of source material, whether concentrates, slags, residues or scraps (Kania et al., 2023)

1.3.1 Zinc ash

Zinc ash is formed on the bath surface as a result of molten zinc oxidation in a contact with air. Zinc ash consists predominantly of crude zinc oxide. It is a by-product of production of Zn. It appears as powder and can be used as raw material for production of ZnSO4, ZnCl2 and ZnO by direct method. The typical elemental composition of zinc ash includes 60-85%Zn, 2-12%Zn, 0.3-2.0%Pb, 0.2-1.5%Fe and up to 0.3%Al (Rudnik et al., 2018).

Figure 2.: Burnt tyre Ash

2.0 Hydrometallurgical Process

Hydrometallurgy is a technique within the field of extractive metallurgy to obtain metals from their ores. Hydrometallurgy involves the use of aqueous solutions for the recovery of metals from ores, concentrates, and recycled of residual materials (Free, 2021). Consideration must be given to both the chemical and physical condition of the zinc waste systems in order to devise successful metallurgical separation processes appropriate for the specific industrial case. Some work has reported at an industrial scale or experimental scale, the recovery of zinc from waste dusts (Xue et al., 2022). One particular scheme is devised for zinc recovery from a fly ash generated by a waste to energy plant (Krishnan et al., 2021). The result presented on a bench scale experimentation to evaluate its technical feasibility and demonstrate its potential for producing marketable zinc product.

Hydrometallurgical metal separation processes provide a number of advantages for application to non-ferrous metal recovery from industrial wastes (Krishnan et al., 2021). These advantages include low energy requirement relative to pyrometallurgical processing, flexibility in processing complete metal mixtures, energy efficient, flexible and applicability to small processing plants, convenience in handling of aqueous systems and minimal environmental problems, such as toxic gas and dust emissions. The Unit processes of hydrometallurgy include the leaching of particularly low-grade ores for the recovery of metals, the separation of leaching solution from the ore and also the recovery of the dissolved metal from the solution.

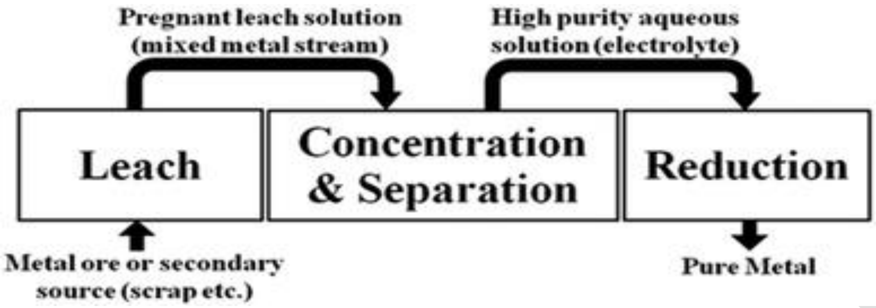

Fig. 3: Hydrometallurgical Process

2.1 Solvent Extraction of Zinc

Zinc is one of the mineral that has been neglected previously, but recently gaining importance as a base metal for various applications in metallurgical and chemical industry (Matinde et al., 2018); it is widely extracted from its primary ore (sphalerite) and can also be recovered from secondary sources (Šajn et al., 2022). Such as zinc ash, zinc dross, flu dust of electric arc and automobile shredder scrap. The chemical nature of the secondary source is such that they are classified as hazardous waste and their toxicity is mainly due to the presence of different of metal such as lead, cadmium, cobalt, arsenic and chromium (Khatun et al., 2022). Therefore, the depletion of the primary sources of metal, researcher have begun to search for alternative which has resulted in metal like zinc now using extracted from secondary sources like galvanizing plant dross and ash, spent primary batteries, zinc scrap, leach residue flue dust generated from iron making and steel making plant however spent galvanizing (Khatun et al., 2022).

A lot of work have been reported in the literature regarding the use of extractant of diverse nature and in various media such as dithizone and cyclohexanones have limited solubility in organic solvents, and so not recommended when zinc concentration is greater than 10−3 mol/L. Carboxylic acids, amines, organophosphorus compounds, and chelex-100 have been cited as good candidates for the extraction of Zn (Khatun et al., 2022).

However, there are a lot of environmental problems associated with the handling of cyanide solutions due to its high toxicity. In the present work, a comparative study was carried out on the effectiveness of 8-hydroxyquinoline (HQ) and triphenylphosphine (TPP) as extractant for zinc (II) from aqueous solution (Fiorani et al., 2021). 8-hydroxyquinoline belongs to the group of compounds with general formula CaHbNeOd. 8-hydroxyquinoline has been reported to be effective for the extraction of palladium in acid medium (Viola et al., 2024) .The extraction is based on complex formation while triphenylphosphine with formula (C6H5O)3P is effective for the extraction of Zn, Cu, Pb, and precious metals in HCI with concentrations (Mehio, 2016). Other extractant such as D2EHPA (Di-2-ethyl hexyl phosphoric acid), TBP (Tributylphosphate) have also been cited to be good candidates for the extraction of zinc (II) in acid media (Sathityatiwat, 2019). Selecting HQ and TPP was based on availability of these extractant. There is practically little or no information on the ability of TPP to extract Pb or Zn, except a report on its use for extraction of palladium (Krishnan et al., 2021).

Zinc ash is an importance secondary sources of zinc recovery as it constitutes sources from which high amount of zinc can be recovered. However, there has been little attention on the metal recovery from combustion ashes derived from tyre wastes. This current project will investigate the metal leaching behaviour of burnt tyre ash and the solvent extraction process using TBP. Pyrometallurgical and hydrometallurgical processes employed in the treatment of secondary sources, are more environmentally friendly and cost effective in treating zinc containing materials through leaching and selective precipitate by solvent extraction (Loy et al., 2018).

Hydrometallurgical process usually involves dissolution of the secondary sources (sometimes after ashing) in an acidic media sometimes with prior water treatment and recovering the zinc from the solution. Ammonium carbonate has been used for zinc recovery from steel dust, automobile scrap and incinerator fly ash (Kaya et al., 2020) in the latter case with a 400 ^{o}C roasting step included. Combination treatments have also been used such as sulphuric acid and chloride leaching with electrogalvanizing dust, waste acid and alkali for fly ash, sulphuric acid and sodium bisulphide/carbonate for flue dust and a combination of acid/oxygen/ H20/ & S20, with blast furnace dust. Sulphuric acid leaching has been used for steel dusts and is the most commonly used approach for the solubilisation of solid zinc waste solids (Binnemans et al., 2020). About 30-40% of zinc consumed comes from reclaim ed zinc sources (Kania *et al*., 2023 ; Kaya et al., 2020). Pyrometallurgical processes generally involves heating at temperature (usually in furnace) the secondary sources of zinc to remove the non-metallic content of the sample and then leaching the zinc rich ash in suitable acid. It is employed in the processing of most of the metal and find application in the extraction of base metal like zinc, tin etc. Extractant such as TBP and Cyanex272 have been used by researchers that exploited the recovery of zinc from spent batteries (Tanong et al., 2017).

2.2 Extractant

Tributylphosphate is an organophosphorus compound with the chemical formula $(CH_3CH_2CH_2CH_2O)_3PO$. It is colourless, odourless liquid finds some application as an extractant and a plasticizer (Jangid *et al.*, 2023). It is an ester of phosphonic acid with n-butanol. It is used as a solvent for extraction and purification of rare earth metal from the ores. The aim of an extractant is to provide high selectivity and efficiency for metal chelation. It also refer to solvating extractant.

2.3 Leaching

Leaching involves the removal of contaminants (organic or inorganic) from a solid-state into a liquid phase when a substance is subjected to different processes such a mineral dissolution, complexation and desorption (Isak *et al.*, 2023). Leaching is one of the important processes involved in the field of metallurgy (Šajn *et al.*, 2022). This is also defined as the process by which a certain valuable soluble fraction is removed from solid phase with which it is associated into a solution.

2.4 Atomic Absorption Spectrophotometry

Atomic absorption spectroscopy was first used as analytical techniques in the second half of 19th century by Robert Bunsen and Robert Kirchhoff. They were led by Sir Alan Waish at the Common Wealth Scientific and Industrial Research Organisation. It is an analytical technique that measures the concentration of an element by measuring the amount of light that is absorbed at a characteristic wavelength when it passes through cloud of atom. Atomic Absorption spectroscopy is a very common technique. It is very reliable and simple to use, It is also measures the concentration of metals in the sample. As the number of atoms in the light path increases The techniques uses basically the principle that free atom generated in an atomizer can absorb radiation at specific frequency. Atomic Absorption Spectroscopy quantifies the absorption of ground state atoms in the gaseous state. The analyte concentration is determined from the amount of absorption. It is widely used in metallurgy alloys and inorganic analysis as of element present in biological sample can be analysed (Kuroda *et al.*, 2023)

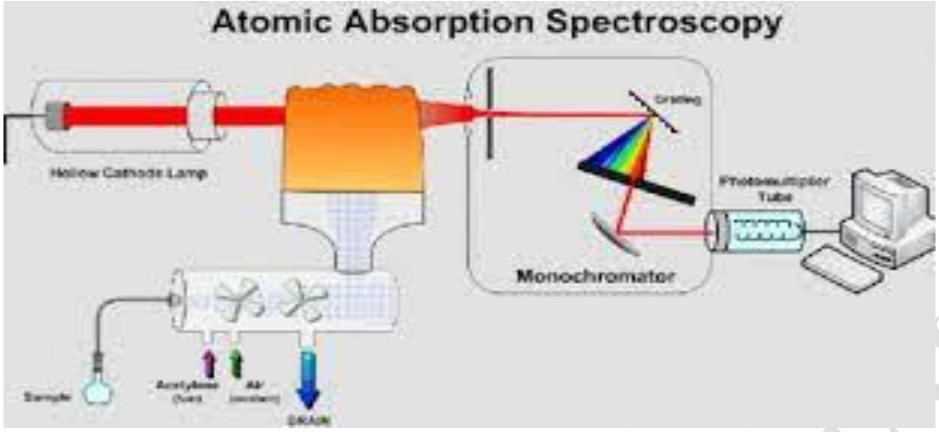

Figure 4 : Instrumentation of Atomic Absorption Spectroscopy

2.5 Significance of the Study

Zinc is an important industrial metal used in various applications, including galvanizing of steel, manufacturing brass and other alloys, as well as in the production of batteries, paints, and fertilizers. (Sabnavis et al., 2018). The global zinc market is influenced by factors such as supply and demand dynamics, global economic conditions, technological advancements, environmental regulations, and geopolitical factors (Sverdrup et al., 2019).

Zinc is widely used in various industries, including construction, automotive, electrical and electronics, and agriculture (Jones et al., 2014 ; Mielcarz-Skalska and Smolińska 2017) ; these drive the demand for zinc ores and zinc products. It is important to note that the specific geology, mineralogy, mining, and processing methods for zinc ores may vary depending on the location and type of deposit, as well as technological advancements and industry practices at a given time.

In 2006, there were consumers over 11 million tonnes of zinc. Of these, 47% were used for corrosion protection of iron and steel products by galvanizing. The most important field of application according to consumption quantities are its alloys, preferably those with copper, such as brass, or with aluminium, either as Al-Zn alloy or with significantly higher zinc contents than Al-Zen, which is used for parts produced in sand casting and chill casting.

Zinc is also contained in the standardized magnesium alloys and is up to 5%. Equally important are the standardized fine-zinc casting alloys, which are cast predominantly in die-casting, but also in sand and mould. Zinc alloys are also processed into rolled material such as zinc sheets. Another possible application of zinc coatings is zinc sprays. Metallic zinc is one of the most important materials for negative electrodes (anodes) in non-rechargeable batteries and is used on an industrial scale. Examples are alkaline-manganese batteries, zinc-carbon batteries, zinc-air batteries, silver oxide-zinc batteries and mercury-oxide-zinc batteries.

Zinc has also been used as an anode in many historical galvanic elements. These include, among others, the Voltasche column, the Daniell element and the Bunsen element. To a lesser extent, zinc is also used for negative electrodes in accumulators (rechargeable batteries), zinc is mixed with small amounts of other metals. These include, for example, lead, bismuth, indium, aluminium and calcium. Zinc die casting is the common name for die-cast parts made of fine zinc casting alloys. These alloys provide far better casting values than are possible, when casting pure zinc. The range of applications includes automotive accessories and those in mechanical and apparatus engineering, also fittings of all kinds, parts for the sanitary industry, for precision equipment and electrical engineering, for metal toys and many household utensils. It was used in times of need, most recently in the two world wars, in the form of zinc alloys for coinage.

Zinc is used in the so-called Solzinc process for the production of hydrogen. Thus, it acts as a reducing agent and as such can be activated in different ways.

An example is the Clemmensen reduction of carbonyl compounds with amalgamated zinc.

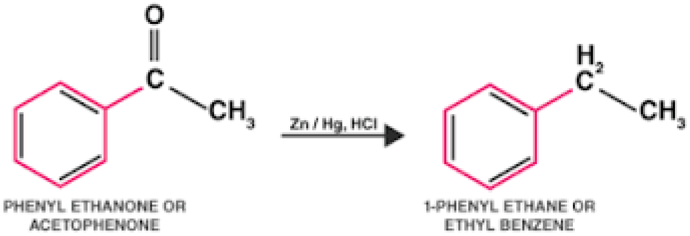

Figure 5: Clemmensen reduction

Galvanized steel is the main sources of secondary zinc, both in the galvanizing process and in the reheating of galvanizing steel. It can be easily recycled with other scrap steel in the electric arc furnace for steel production.

3.0 MATERIALS AND METHODS

3.1 Material and equipment

- Filter Paper
- Conical flask
- Measuring cylinder
- Separating funnel
- Funnel
- Hot plate (85-2, USA)
- Beaker
- PH meter (HANNA pH 210)
- Fume cupboard
- Magnetic stirrer (85-2,USA)
- Reagent bottles
- Volumetric flask
- Thermometer
- Atomic Absorption Spectroscopy (AA280FS, USA)

3.2 Reagent:

Reagents used for this research were of analytical grades and the leachants used for the experiments was Hydrochloric acid. NH_4OH was used to raise the pH of the acidic liquid while HCL was used to lower the pH of the basic liquid and distilled water was used for the preparation of all solutions used.

3.3 Sample Collection

Burnt tyre ashes (1 kg) were collected from waste dumpsite at Dogarawa area, Zaria, Kaduna state, Nigeria in November, 2022. Tyres were burned following confiscation by a regulatory agency.

3.4 Methods

Ash (2.5 g) was dissolved in aqua regia (250 ml) at an ambient temperature of 25 °C for less than 2 hours (1:3 of HCl: HNO_3) and the total concentration of zinc in the ash was measured in the resulting solution by Atomic Absorption Spectrophotometry after filtration and dilution.

3.5 Determination of Total Zinc Content in the Dumpsite Ash and Optimum Leaching Condition for Zinc

The optimum leaching condition of HCl concentration, temperature, leaching time and agitation speed were determined in the previous experiment and are; 2.968 mol/L of HCl, 68.85$°C$, 97.703 minutes, at agitation rate of 400rpm and the amount of zinc leached was 32009.205 mg/L.

3.6 Preparation of Hydrochloric acid solution

Where, Molar mass of HCl = 36.5g/mole

% Purity = 37,

Specific gravity = 1.18 g/cm^3

$$\boxed{M = \frac{\%P \text{ X } Spg \text{ X } 10}{Mm}}$$

M = molarity, Spg = specific gravity, Mm = molar mass

Calculation

$$M = \frac{\%P \times Spg \times 10}{Mm}$$

$M = \frac{37\times1.18\times10}{36..5}$

M =11.96M

This is the molarity of the stock HCl solution by dilution formula

$C_1V_1=C_2V_2$

The concentration 2.968 mol/L can be prepared

$V_1=\frac{C2\times V2}{C1}$

$V_1= \frac{2.968\times250}{11.96}$

$V_1=62.04\ cm^3$

Optimum concentration of 2.968M HCl was prepared by measuring in 62.04 cm^3 into a measuring cylinder and added to 30 ml of distilled water contained in a 250 cm^3 volumetric flask and made up to the 250cm^3 mark with distilled water.

3.7 Leaching of Zinc from the Dumpsite Ash

2.5 g of burnt tyre ash was weighed and introduced into a 250 cm3 prepared solution of HCl in a 500 cm3 beaker and was introduced on a heating magnetic stirrer at 68.85°C. A magnetic stirrer bar was inserted and the solution was covered with glass lid. The burnt tyre was left to be in contact with the lixiviant for 97:703 minutes, at the end of the contact time, the mixture obtained was then filtered and the insoluble residue left on a filter paper was washed thoroughly with a little of the hot filtrate. The filtrate was then carefully transferred into a 250ml standard volumetric flask. The solution was made to mark with distilled water; the filtrate in the standard volumetric flask was then adjusted to pH 3.5 with a pH meter before analysis, using Atomic Absorption Spectroscopy (AAS) as presented in plate .1.

Plate.1 : Preparation of leach liquor

3.8 Preparation of TBP solution

Tributylphosphate $(CH_3CH_2CH_2CH_2O)_3PO$ has an essay % Purity = 99%, Specific gravity = 0.98 g/cm^3, Molar mass = 266 g/moL

Calculation of molarity of the stock TBP

$$M = \frac{\%P \times Spg \times 10}{Mm}$$

$$M = \frac{99 \times 0.98 \times 10}{266}$$

M = 3.65M (concentration of the stock TBP)

Using dilution formula, volume of TBP needed to prepare a standard solution can be calculated;

$$C_1V_1=C_2V_2$$

To prepare 0.30M TBP

$$V_1 = \frac{0.30 \times 50}{3.65}$$

$V_1 = 4.10\ cm^3$

About 4.10 cm^3 of TBP was measured and slowly added to 25 cm^3 kerosene in a 50cm^3 volumetric flask and made up to the 50 cm^3 volume with kerosene.

The same process was carried out for the preparation of other concentration of TBP which were 0.05M, 0.10M, 0.15M, 0.20M, 0.25M and 0.30M

3.9 Procedure for the solvent extraction of Zn from leach liquor

The experiment was performed using the leachate obtained by the optimal conditions of the temperature leachant, concentration and time of zinc in the leached liquor in section 3.7 and analysis was carried out by AAS at room temperature 25±2°C. Equal volume 10 cm^3 of the predetermined concentration of the extractant (TBP) which were 0.05M to 0.30M TBP with 10 cm^3 of leachate from section 3.7 were mixed in a 250 cm^3 conical flask and shaken using mechanical shaker for 25 minutes at room temperature. The pH of the pregnant leach solution in each case was ensured to be pH 4.5. Plate.2 presents the preparation of the aqueous and organic phases.

PLATE.2 : Preparation of aqueous phase and organic phase

After the equilibration phase disengagement was carried out for each experimental group in 250 cm^3 separating funnel, it was allowed to form two separation layers. The upper one contained Zn loaded organic phase while the lower part had a clear solution, after the formation of two distinct layers the clear solution (aqueous phase) was drained out by opening the tap. The concentration of Zn in each experimental group of TBP concentration was calculated using AAS analysis, to determine the Zn composition left in the aqueous phase.

Plate.3: Separating funnel setup

The concentration of the metal in an organic phase was calculated from the differences between its concentration in the aqueous phase before and after the extraction (Yamada *et al.*, 2023). Then % Zn extracted against TBP concentration was plotted.

3.10 Effect of pH on the Solvent Extraction of Zinc

The percentage of extracted Zn against concentration of TBP that gave the highest percentage of co-extracted was used for optimization of other parameter which included equilibrium pH of the aqueous media (Mohammadzadeh *et al.*, 2022). The pH of the leach liquor in section 3.7 was adjusted to a pH 2.5, 4.5, 5.5 and the % of zinc extracted using solvent extraction, was repeated for each case as in section 3.9. The optimum pH was then determined. A plot of % zinc extracted against pH was plotted.

$$\%\ E= \frac{[M]org}{[M]aqu.initial}$$

$$D = \frac{[M]org}{[M]aqu}$$

Equation of chemical reaction

$$Zn^{2+}_{(aq)} + HCl + 2TBP_{(o)} \longrightarrow Zn(Cl)_2\ TBP)_2 + H^+$$

3.11 Stripping of zinc

Stripping of Zn from the loaded organic phase was carried out by contacting the experimental organic phase with 0.05mol/L HCl solution and shaken for 25 min thereafter; the mixture was allowed to reach equilibrium and then separated with a separating funnel

4.0 RESULT AND DISCUSSION

Table .1: Effect of TBP concentration on the amount Of zinc unextracted from the leached liquor

S/N	[TBP]/pH	[Zn] (ppm)	SD	Mean Abs
021	[0.05M] at pH 2.5	2.2353	0.0033	0.3635
018	[0.10M] at pH 2.5	1.7878	0.0036	0.2907
016	[0.15M] at pH 2.5	1.7074	0.0053	0.2777
020	[0.20M] at pH 2.5	1.6981	0.0019	0.2761
017	[0.25M] at pH 2.5	1.6511	0.0028	0.2685
019	[0.30M] at pH 2.5	1.6107	0.0027	0.2619
025	[0.05M] at pH 3.5	2.5260	0.0105	0.4108
026	[0.10M] at pH 3.5	2.4873	0.0024	0.4045
022	[0.15M] at pH 3.5	2.4571	0.0045	0.3996
027	[0.20M] at pH 3.5	2.4092	0.0063	0.3918

023	[0.25M] at pH 3.5	2.3516	0.0060	0.3824
024	[0.30M] at pH 3.5	2.2809	0.0085	0.3709
001	[0.05M] at pH 4.5	1.7656	0.0061	0.2871
002	[0.10M] at pH 4.5	1.6340	0.0059	0.2657
003	[0.15M] at pH 4.5	1.6292	0.0043	0.2650
004	[0.20M] at pH 4.5	1.5012	0.0036	0.2441
005	[0.25M] at pH 4.5	1.4420	0.0055	0.2345
006	[0.30M] at pH 4.5	1.3042	0.0055	0.2121
009	[0.05M] at pH 5.5	1.9604	0.0092	0.3188
010	[0.10M] at pH 5.5	1.8855	0.0109	0.3066
011	[0.15M] at pH 5.5	1.5793	0.0014	0.2568

012	[0.20M] at pH 5.5	1.4508	0.0012	0.2359
013	[0.25M] at pH 5.5	1.4348	0.0002	0.2333
014	[0.30M] at pH 5.5	1.4247	0.0027	0.2317

CALCULATION

Formula for leaching

Actual concentration = Instrument reading x Dilution factor

For aqueous initial

Instrument reading = 2.5477ppm,

Dilution factor -100

Actual concentration – 254.77mg/L or 254.77ppm

The initial concentration of zinc in the leached gotten was 254.77mg/L

Table .2: Effect of concentration of TBP against % Zinc Extracted into organic phase at pH 2.5

TBP concentration	Instrument reading	Actual conc.(ppm)	[M]org	% E	Distribution ratio (D)
0.05M	2,2353	223.53	31.24	12.26%	0.139
0.10M	1.7876	178.76	76.01	29.83%	0.423
0.15M	1.7074	170.74	84.03	32.98%	0.492
0.20M	1.6981	169.81	84.96	33.35%	0.500
0.25M	1.6511	165.11	89.66	35.19%	0.543
0.30M	1.6107	161.07	93.70	36.79%	0.582

Table 3: Effect of concentration of TBP against % Zinc Extracted into organic phase at pH 3.5

TBP concentration	Instrument reading	Actual conc. (ppm)	[M]org	% E	Distribution ratio
0.05M	2.526	252.6	2.17	0.88%	0.089
0.10M	2.4873	248.73	6.04	2.37%	0.024
0.15M	2.4571	245.71	9.06	3.55%	0.037
0.20M	2.4092	240.92	13.85	5.20%	0.057
0.25M	2.3516	235.16	19.61	7.69%	0.083
0.30M	2.2809	228.09	26.68	10.47%	0.117

Table 4: Percentage of zinc extracted into the organic phase with TBP concentration at pH4.5

Concentration TBP	Instrument reading	actual conc. (ppm)	[M]org	% E	Distribution ratio (D)
0.05M	1.7656	176.56	78.21	30.69%	0.443
0.10M	1.634	163.4	91.37	35.86%	0.559
0.15M	1.6292	162.92	91.85	36.05%	0.564
0.20M	1.5012	150.12	104.65	41.08%	0.697
0.25M	1.4421	144.21	110.57	43.39%	0.767
0.30M	1.3042	130.42	124.03	48.68%	0.947

Table .5: Effect of concentration of TBP against % Zinc extracted into organic phase at pH 5.5

TBP concentration	Instrumental reading	Actual concentration	[M]org	% E	Distribution ratio
0.05M	1.9604	196.04	58.72	23.05%	0.299
0.10M	1.8855	188.55	66.22	25.99%	0.351
0.15M	1.5793	157.93	96.84	38.01%	0.613
0.20M	1.4508	145.08	109.65	43.04%	0.756
0.25M	1.4348	143.48	111.29	43.68%	0.776
0.30M	1.4247	142.47	112.3	44.08%	0.762

Table .6: Summary of the effect of concentration of TBP against pH of the extraction of Zinc

Concentration of TBP	pH 2.5	pH 3.5	pH 4.5	pH 5.5
0.05M	0.139	0.024	0.443	0.299
0.10M	0.423	0.037	0.559	0.351
0.15M	0.492	0.057	0.564	0.613
0.20M	0.500	0.087	0.694	0.756
0.25M	0.543	0.089	0.767	0.762
0.30M	0.582	0.117	0.942	0.776

Table 7: Effect of concentration of TBP against Distribution ratio

Concentration of TBP	log x	Distribution ratio	log D
0.05M	-1.30103	0.206	-0.68613
0.10M	-1	0.343	-0.46471
0.15M	-0.82391	0.436	-0.36051
0.20M	-0.69897	0.508	-0.29414
0.25M	-0.60206	0.539	-0.26841
0.30M	-0.52288	0.604	-0.21896

Where x = [TBP]

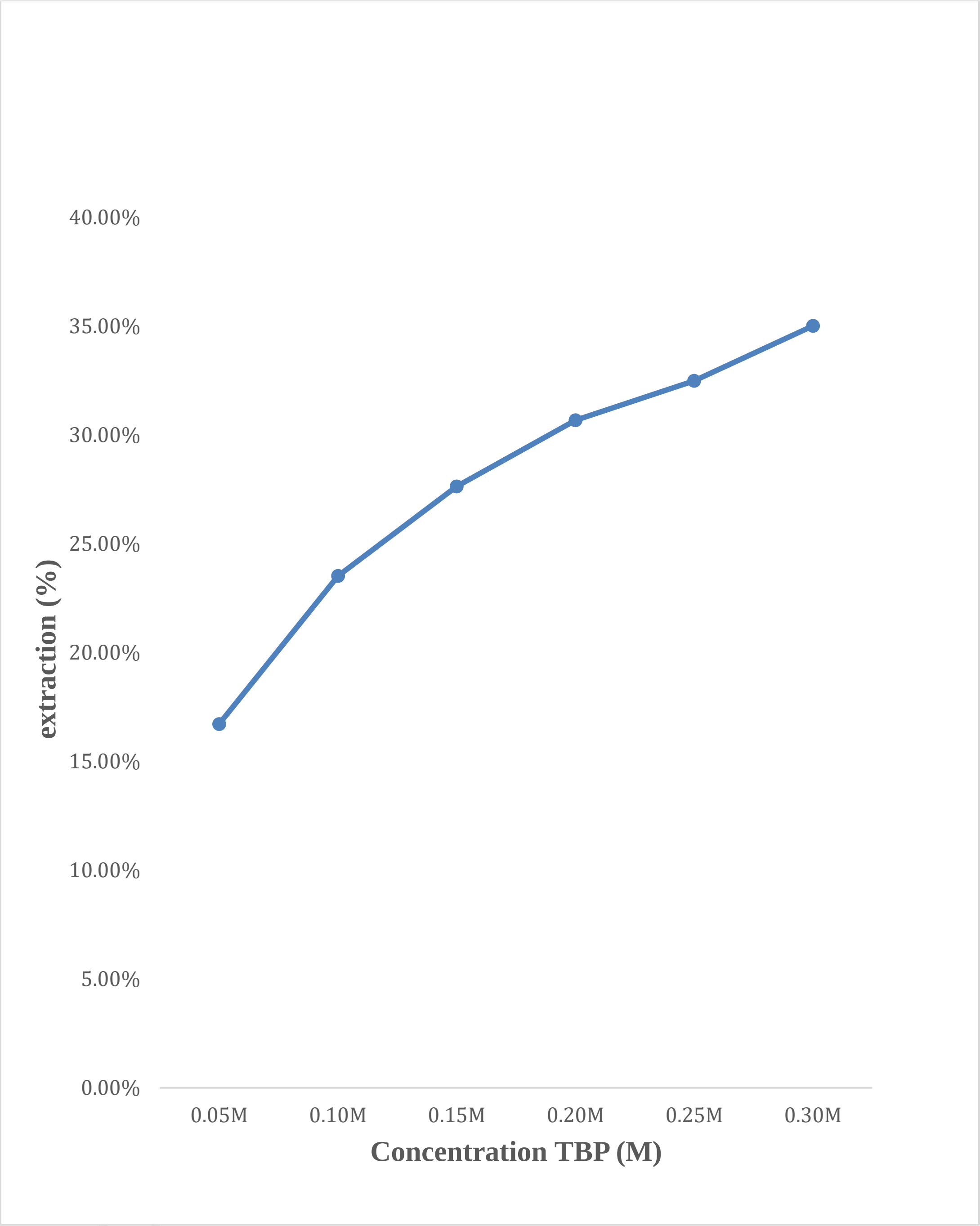

Figure 6: Plot of % of zinc extracted against concentration of TBP

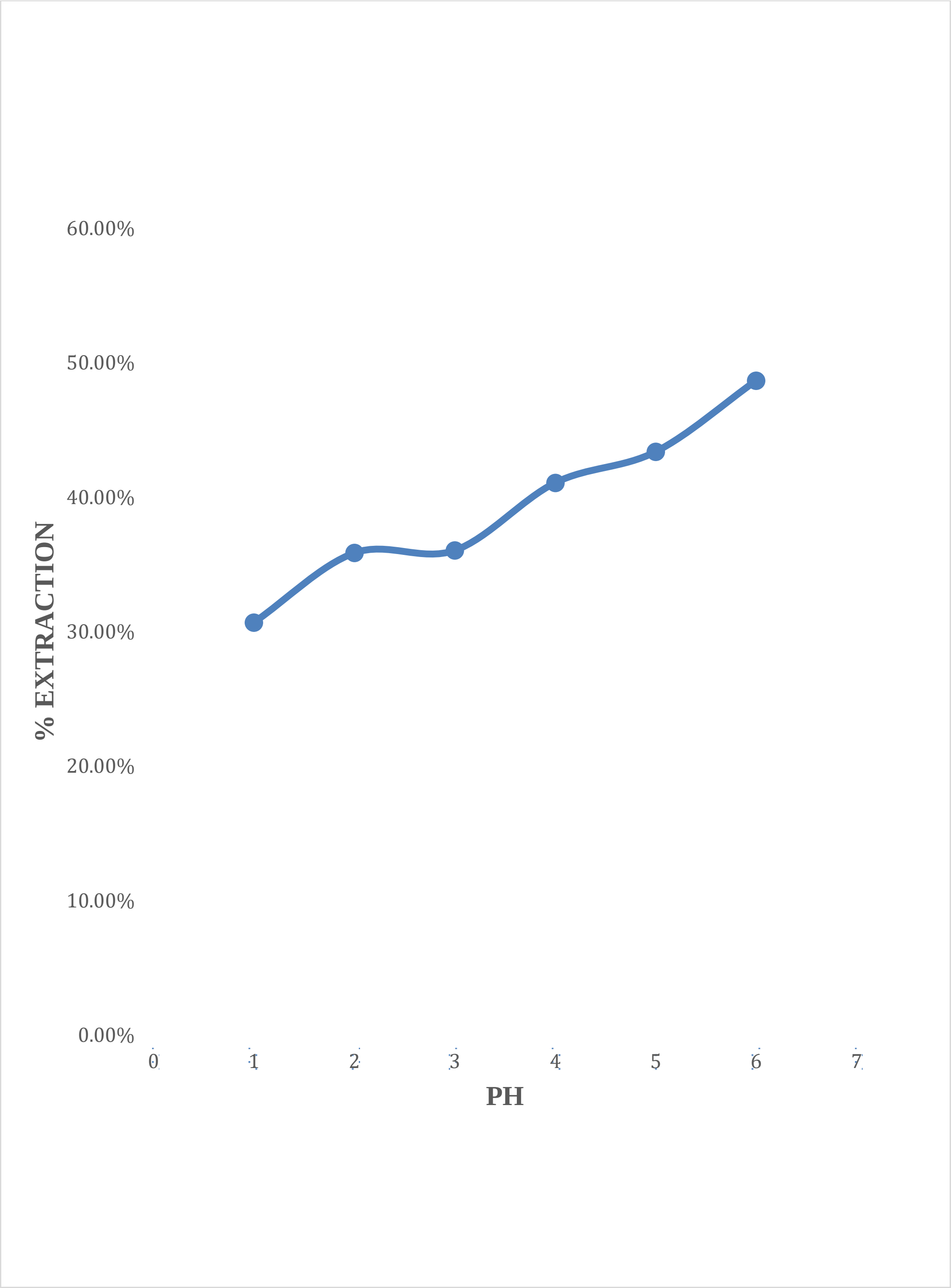

Figure 7: Effect of pH % of zinc extracted

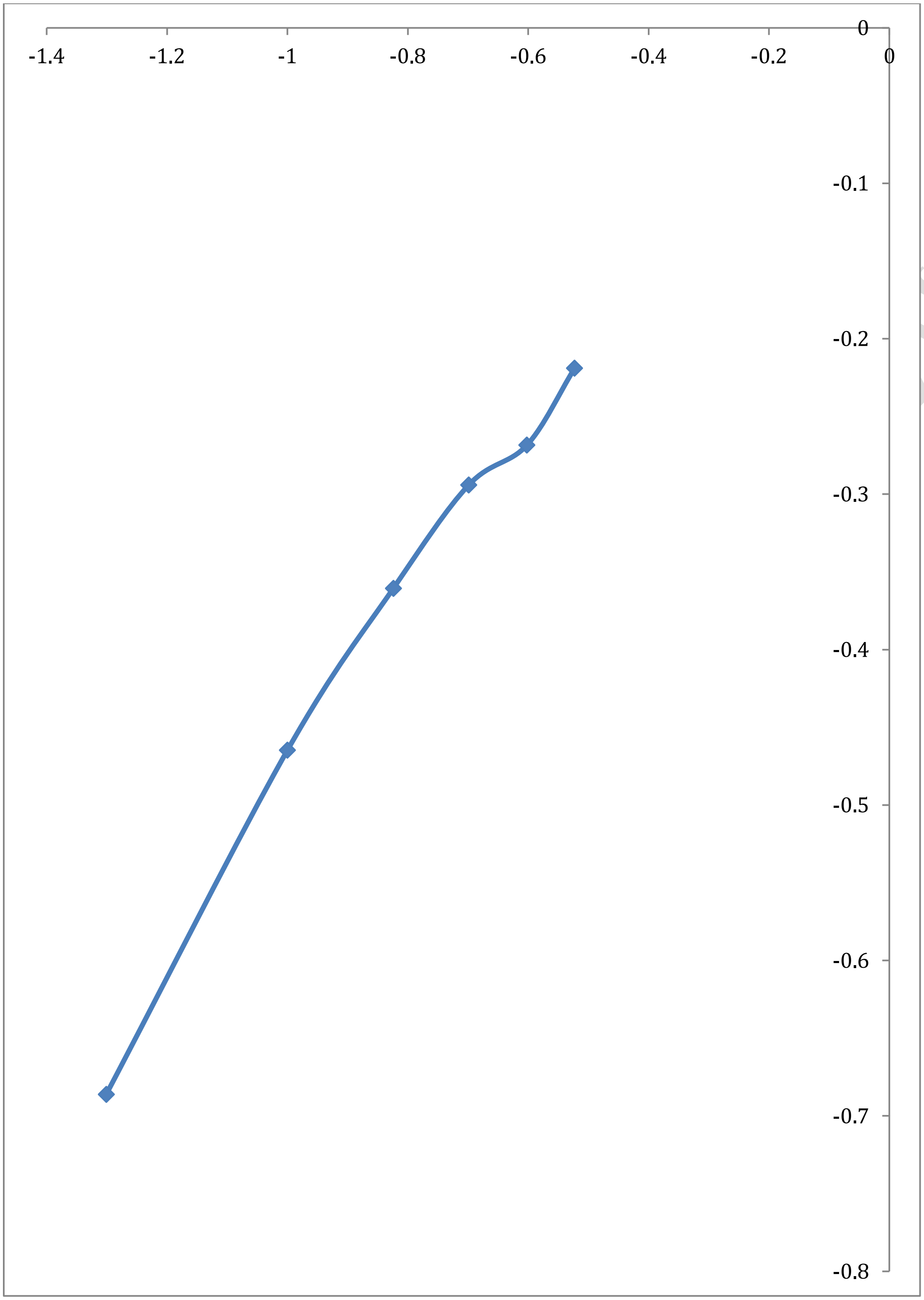

Figure 8: plot of log D against log [TBP]

4.1 Effect of TBP concentration on the extraction of zinc from burnt tyre ash

The initial concentration of zinc in the leached liquor gotten was 254.77mg/L. The effect of the extractant concentration on the extraction of zinc from the leached liquor was carried out over TBP concentration range of 0.05-0.30mol/L at pH of 4.5.The results obtained in Table .1 showed that the percentage of zinc extracted increased with increase in the extractant concentration. Thus, a plot of the percentage of zinc extraction against the TBP concentration was gotten, to get the optimal TBP concentration. The highest percentage of zinc extracted was 48.68% using 0.30M TBP at pH 4.5

4.2 Effect of TBP concentration on distribution ratio

The effect of TBP concentration on the distribution ratio D, of zinc was also studied and the result given in Table .2, increased from 0.443 to 0.947. The distribution ratio increased with an increasing extractant concentration. The slope of the plot of log D against log TBP in Table .6 and figure 8 gave 1.32 and indicated that 1 mole of the extractant was involved in the extraction process. One mole of $[H^+]$ from the extractant, TBP was exchanged for one mole of Zn^{2+} at each process of the extraction of zinc from the burnt tyre ash obtained from Dogarawa, Zaria, Nigeria.

4.3 Effect of pH on the extraction process

The effect of pH on the extraction process was studied with [TBP] over equilibrium pH range of 2.5, 3.5, 4.5 and 5.5 (Table 6). The effect of pH was logged in the amount of zinc extracted by TBP. The percentage of zinc extracted plotted against pH. It was observed that the percentage of extracted zinc from the burnt tyre ash was increased with increase in the pH of the aqueous phase, with maximum extraction observed at pH 4.5, being 48.68% in figure 7 (Table .1)

4.4 Effect of TBP concentration

A plot of log D against log [TBP], was also observed that D value increased with an increase in [TBP] and was plotted in figure 8. A linear plot with a slope of 0.60 ~ 1, was obtained in figure 7 and apparently indicated the liberation of one mole of $[H^+]$ during extraction of one mole of Zn^{2+} from the burnt tyre ash. Figure 8 for plot of log [TBP] against log D is linear.

4.5 Stripping studies

The stripping study of zinc from the loaded TBP was carried out with dilute HCl solution. The result of the stripping investigation showed that 0.05mol/L HCl stripped zinc from the loaded TBP at a 1: 1 phase ratio.

5.0 CONCLUSION

- Therefore, based on the result obtained, the following conclusion can be expressed as the result obtained in the solvent extraction of zinc by TBP in kerosene indicated that an increase in the initial extractant concentration (organic phase) enhanced the extracted percentage of zinc from burnt tyre ash with the highest percentage of zinc being 48.68% by 0.30 mol/L TBP at pH 4.5.
- Liquld-Liquld Extraction of Zn^{2+} using Tributylphosphate in kerosene was found to have the potential of extracting zinc from burnt tyre ash leach liquor at optimum condition with one mole of $[H^+]$ being liberated during extraction of one mole of zn^{2+} from the burnt tyre ash.
- The study showed that a phase ratio of 1:1 for the organic phase ; aqueous phase extracted 48.68% of the total zinc into the organic phase at a pH of 4.5 and 60% of the loaded organic phase was quantitatively stripped by 0.05mol/L.

ETHICAL APPROVAL

As per international standards or university standard written ethical approval has been collected and preserved by the author(s).

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that no generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

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