LIQUID-LIQUID EXTRACTION OF Co(II) FROM AQUEOUS SOLUTION: A SHORT REVIEW

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A

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CERTIFICATE I

This is to certify that the thesis entitled **"Liquid-Liquid Extraction of Co(II) from Aqueous solution: A Short Review"** submitted in partial fulfilment of the requirements for the award of the degree of MASTER OF SCIENCE IN CHEMISTRY of Odisha University of Agriculture and Technology, Bhubaneswar is an authentic record of bonafide research work carried out by **NIRANJANA DAS** under my guidance and supervision. No part of the thesis has been submitted for any other degree or diploma.

It is further certified that the evidence and help obtained by her from various sources during the course of investigation have been duly acknowledged.

Place: **CHAIRMAN**

Date: **ADVISORY COMMITTEE**

CERTIFICATE II

This is to certify that the thesis entitled "**Liquid-Liquid Extraction of Co(II) from Aqueous solution: A Short Review"** submitted by **NIRANJANA DAS** to Odisha University of Agriculture and Technology, Bhubaneswar in partial fulfilment of the requirements for the award of the degree of MASTER OF SCIENCE IN CHEMISTRY has been approved by the students' Advisory Committee and the examiner.

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ABSTRACT

A large volume of waste is generated due to rapid growth of mining and metallurgical industries and the dissolution of heavy metals pollute the industrial belt water. Mostly copper, zinc, cadmium, arsenic, lead, nickel, cobalt etc. are responsible for environmental pollution. So, they should be removed before being discharged to surface water. In terms of metals, cobalt is the most widely used due to its wide range of applications and in human metabolic processes. In excess, however, it can have a number of toxic effects on the ecosystem's flora and fauna. This technique is widely used in hydrometallurgical processes for the removal and separation of ions after leaching, and it is capable of producing pure metal solutions that are used in electrowinning processes. Both concentrated and diluted solutions can be treated with these techniques. The current study examines the extraction of Co(II) using a liquid-liquid extraction method by researchers using various extractants, as well as the relationshipbetween various parameters and the extraction efficiency of the extractants used.

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Finally, I bow my head before the Almighty, whose omnipresence has always led and assisted me in overcoming all ups and downs.

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CHAPTER-1

INTRODUCTION

INTRODUCTION

As a result of man's actions, environmental pollution alters our surroundings in a negative way [1]. Global environmental pollution is primarily caused by human activities such as urbanisation, industrialisation, mining, and exploring [2]. Air, water, and soil contamination make it a severe threat to biodiversity, ecosystems, and human health globally [3]. The industrial wastes, discharged into local streams and lands result in environmental pollution [4]. Metallic contaminants pose a serious threat to the environment because they are non-biodegradable. By virtue of their widespread use, metals have a substantial public concern [6,7] as reported by WHO [World Health Organization].

Cobalt is most popular of metals and an essential trace element. Because of its appearance, hardness, and resistance to oxidation, cobalt is utilised in electroplating. Cobalamin, generally known as vitamin B12, has it as a significant component [8]. Excess concentration of cobalt may cause genetic and metabolic disorders and produces toxic effects like polycythemia and hyperglycemia with transitory damage to pancreatic alpha cells [9]. As a result, industrial wastes must be properly handled before disposal [10]. It is possible to handle metallic hazardous wastes in several ways, which contain adsorption and co-precipitation. It also include electrochemical deposition ion exchange solid phase extraction and others [11]. Due to its excellent repeatability. liquid-liquid extraction is a cost-effective techniques for the treatment of metal-containing waste. It's a very clever, inexpensive, and rapid solution that's easy to use. In both diluted and concentrated solutions, it allows for therecycling of metal ions[12].

Our work attempts to provide insight on how cobalt is extracted, which can be reused for a variety of additional applications. These superalloys, which are

used in turbine blades and aviation engines, utilise the majority of the cobalt produced. Magnets are made from cobalt because it can be magnetised. Aluminium and nickel are alloyed with niobium to create extremely powerful magnets. Because of its appealing look, hardness, and corrosion resistance, it is employed in electroplating processes. When it comes to vitamin B12, Co is an useful trace component[13].

In recovery of Co(II) TOPO, an organic complexing agent, was utilised as an analytical reagent In addition to TOPO, the chemical compound trioctylamine (TOA), which belongs to the aliphaticamines and tertiaryamines family, has been utilised to extract cobalt. The octyl groups make low polarity solvents like kerosene, toluene, etc. solubilized [14].

Using alamine 336-m-xylene combinations, Filiz *et al*.[15] were able to recover cobalt(II). An extractant for Co was found to be Alamine 336 mixed with meta xylene (II). Parallel to this, the dynamics of extractant volume – domain were studied. A mathematical model has been constructed and the optimal Alamine 336 content for one stage extraction was determined.

Hydroxamic acids were used in the solvent extraction of cobalt by Monzyk *et al.*[16]. Aqueous cobalt solutions are reversibly extracted using solvent extraction procedures by contacting the solution with a hydrocarbon solvent that contains N-alkylakanohydroxamic acid that has at least 8 carbon atoms, and the cobalt is recovered. An entirely new cobalt complex family is also described.

In a study by Banerjee *et al*.[17], ß-hydroxyl napthaldoxime and neutral donors were used to extract Cobalt (II) in synergy. It was found that the average pH

range for Co(II) extraction by ligand-donor combination was 8-9 Diverse diluents and donors, such as dimethyl sulphoxide (DMSO), tri-n-octoxyphosphineoxide (TOPO), and bis(2-ethylhexyl) phosphonate, were explored in depth in order to obtain Co(II). There was a clear trend in equilibrium constants, i.e. (DMSO>TOPO=phosphonate). In order to determine the amount of Cobalt in medicinal medications and cobalt containing ore samples, the data were extrapolated.

According to Allal *et al*.[18], tributylphosphate, tri-n-octylphosphineoxide (TOPO), and decanol were used to extract Titanium from chloride medium. HCl and CaCl2 were investigated in both organic and aqueous phase. The equilibration time was attained in 3mins. As the total chloride concentration increase so does the extraction of titanium, Ti(IV).

According to Adjel *et al*.[19], copper(II) can be extracted from sulphate media using capric acid[HL] and tri-n-octylphosphineoxide (TOPO). $CuL_2(HL)_2$ is the recovered product utilising capric acid. $CuL_2(HL)_2$(TOPO) isthe extracted compound in presence of tri-n-octylphosphineoxide (TOPO).The interaction between TOPO and HL has a significant impact on the efficiency of extraction of Cu(II).

CHAPTER-2

THEORETICAL BACKGROUND

THEORETICAL BACKGROUND

2.1 LIQUID-LIQUID EXTRACTION

Two immiscible liquids are kept in contact and the distribution of a chemical component between the two phases is examined using liquid-liquid extraction. According to its solubility and phase volume, a substance's distribution is determined by its distribution. This approach is used in analytic separation methods, such as chromatography. Both macro and tracer concentrations can be separated more easily and more cleanly. In addition to liquid-liquid extraction, solvent extraction is also referred to as solvent extraction. There are two liquid phases in a biphasic liquid system: an organic phase that includes the extracting agent and sometimes diluents, and an aqueous phase which contains the metal ion. In order to boost the extractant's ability to extract, diluent is utilised. In industrial applications, a component termed a modifier is sometimes added to the organic phase in order to eliminate third phase formation. But this is not a common practise. Pharmaceutical industries, organic synthesis, biomolecular processes, petrochemical industries, etc. all use liquid-liquid extraction to a large extent. Continuous and multistage extraction systems are employed for quantitative nuclear material recovery. Peligot *et al.*[20] presented the first report on liquid-liquid extraction of uranyl nitrate with diethyl ether as solvent in 1842[21]. Liquid-liquid extraction techniques have been evaluated by numerous researchers in terms of their principles, applications, and breadth. Among them are Morisson .[21].,Marcus.[22]., De .[23]., Sekine .[24]., Ritcey .[25]., Rydberg .[26]., Sahu .[27] Rice .[28]., Shmidt .[29].

2.2 PRINCIPLES OF LIQUID-LIQUID EXTRACTION

Distribution law

The Nernst partition isotherm governs the distribution of a solute[30]. After reaching equilibrium with the solute, if it has the same molecular form in both aqueous and nonaqueous phases, it will have a constant concentration ratio. In order to calculate the distribution ratio or partition coefficient, we use the formula

$$D = \frac{[M]_{org}}{[M]_{aq}} \qquad \textbf{(2.1)}$$

Equation (2.1) is followed by

$$D = \frac{[M]_{org}}{[M]_{aq}} . \frac{\gamma_2}{\gamma_1}, \qquad \textbf{(2.2)}$$

The distribution ratio is defined as follows:

$$D = \frac{[M_1]_{org} + [M_2]_{org} + ... + [M_n]_{org}}{[M_1]_{aq} + [M_2]_{aq} + ... + [M_n]_{aq}}, \qquad \textbf{(2.3)}$$

Where M_1, ……$M_n$are the various forms of the solute. The distribution ratio is a number with no unit. It establishes the scope of the extraction. The extraction method is determined by the magnitude of the distribution ratio.

Percentage of extraction

Extraction is measured as a percentage of the total amount extracted, or percent E. This is how it's defined:

$$\%E = \frac{V_{org}[M]_{org}}{V_{org}[M]_{org} + V_{aq}[M]_{aq}} \times 100, \qquad \textbf{(2.4)}$$

If the phase volume ratio is reduced to unity, eq.(2.4) will be

$$\%E = \frac{100D}{\left[D + \left(\frac{V_{aq}}{V_{org}}\right)\right]} = \frac{100D}{(D+1)} \qquad \textbf{(2.5)}$$

The kinetics of the extraction system varies based on the method of extraction and the nature of interaction between the various components in the system.

2.3 EXTRACTANTS AND THEIR CLASSIFICATIONS

The qualities of chemical reagents used as commercial extractants should be as follows:

1)Molecular mass is large.

2)Aqueous solubility is low.

3)Metal loading capacity is high.

4)In aliphatic and aromatic diluents, it has a high solubility.

5)Non-toxic, non-flammable, and non-volatile.

The extractants are divided into three categories based on their unique properties: chelating, liquid ion-exchanger, and solvating solvents.

Chelating extractants

Coordination aids in metal ion charge neutralisation and so fulfils its coordination need. On the other hand, if the charge neutralisation requirements are not met, water molecules occupy the unoccupied coordination sites, making the complex more hydrophilic and reducing the amount of extraction. Chelating agents are bivalent and generate cyclic compounds in most cases. Because they are thermodynamically stable, five or six membered rings are preferred. The

coordination atoms of these extractants' functional groups include oxygen, nitrogen, and sulphur.

LIX, SME, Acorga, and Kelex reagents are commercial chelating extractants. The -diketones are a type of -diketone.

Liquid-ion-exchangers

Liquid cation exchangers and liquid anion exchangers are two types of liquid cation exchangers.

(a) Liquid cation exchangers

Because of their capacity to donate proton, these are also known as acidic extractants.

Through a series of processes, they remove metal ions.

$$M^{n+}{}_{(aq)} + nHA_{(org)} \rightleftharpoons MA_{n(org)} + nH^{+} \qquad \textbf{(2.6)}$$

This group includes organophosphorus acids, monocarboxylic acids, and flurocarboxylic acids.

(b) Liquid anion exchangers

Anion exchangers are typically high molecular mass amines. Prior to extraction, aminesare protonated into amine salts, and then anion exchange is used to extract the anionic metal species.

$$R_3N + HX \rightleftharpoons R_3N^{+}HX^{-} \qquad \textbf{(2.7)}$$

$$MA_m^{n-} + nR_3N^{+}HA \rightleftharpoons (R_3N^{+}H)_nMA_m^{n-} + nA^{-} \qquad \textbf{(2.8)}$$

Alamine 300 tri-n-octyl amine, Alamine 304 tri-lauryl amine, Alamine308 tri-isooctyle amine, and others are examples of anion exchangers.

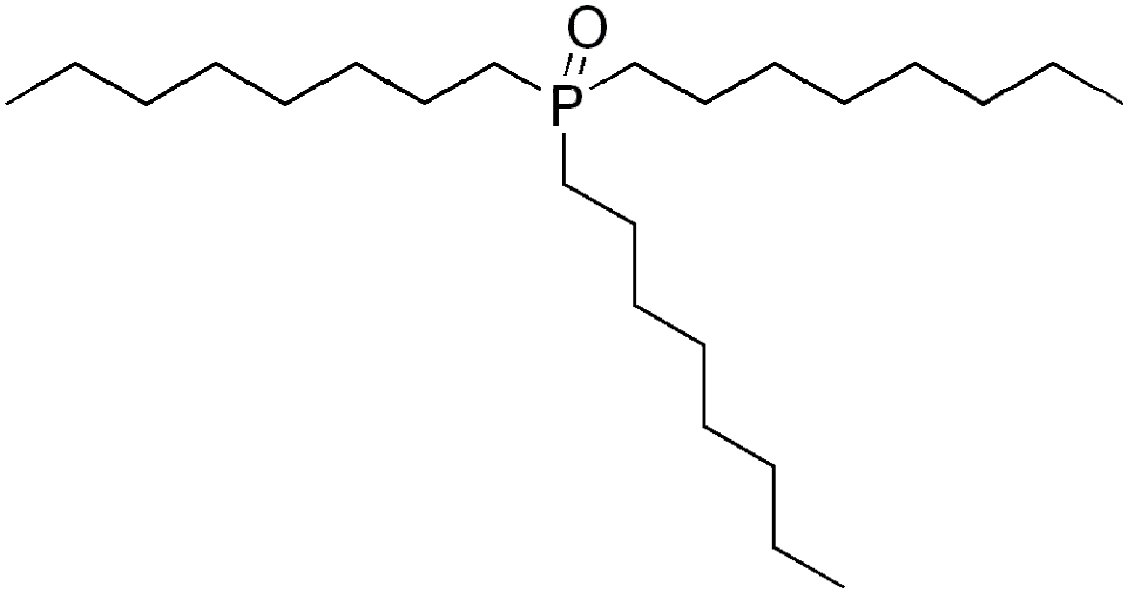
Solvating solvents

These are uncharged metal complexes that are extracted from organic solutions using neutral ligands. The loss of water molecules from the hydration sphere causes the metal complex to solvate, making it more hydrophobic and thus facilitating extraction. This group of extractants includes TOPO, TBP and long-chain-dialkylsulphoxides. Neutral extractants include multifunctional organophosphorousextractants, phosphine sulphides, amides, carbamoyl methyl phosphonate (CMPO), and phosphine oxides.

2.4 EXTRACTANTS USED FOR EXTRACTION OF Co(II) BY THE METHOD OF LIQUID-LIQUID EXTRACTION IN OUR LABORATORY

The extractant used for extraction of Co(II) in our laboratory is Tri-n-octyl phosphine Oxide [(TOPO), $OP(C_{18}H_{17})_3$]. At room temperature, it is an air-stable white solid. Tri-n-octylphosphine oxide is a solvating extractant that is excellent for heavy metal extraction in the liquid-liquid extraction technique. High lipophilicity and polarity are important qualities for this application. The dipolar phosphorus – oxygen connection gives this moleculeits high polarity,which allows it to bind to metal ions. Low polarity solvents like kerosene, toluene, and others are soluble because of the octyl groups [31]. It has a molar mass of 386.645g/mol. At 760 mm Hg, it has a melting point of 50-54°C and a boiling point of 411.2°C.

2.5 STRUCTURE OF TOPO

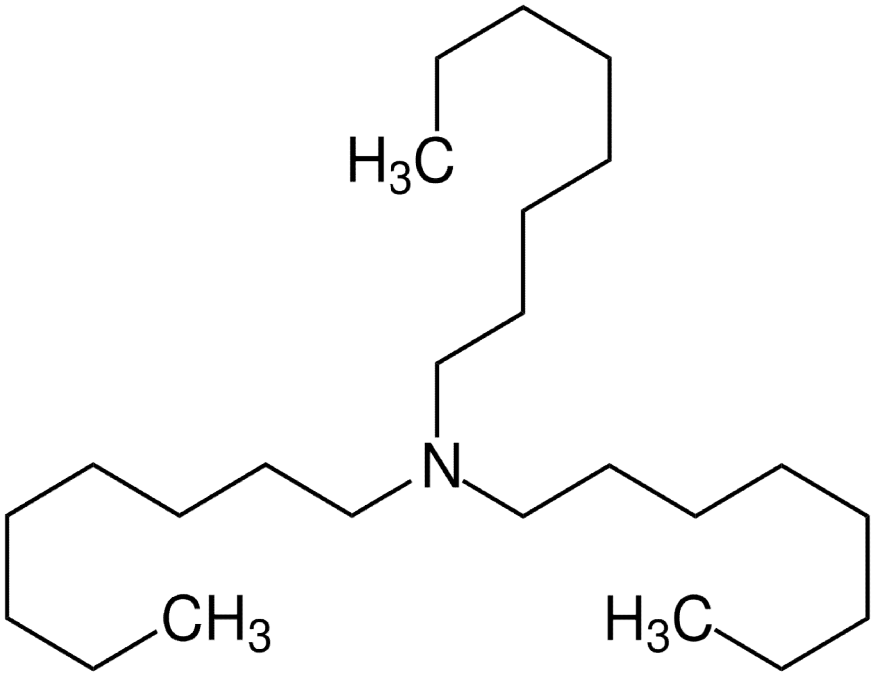


Tri-n-octylphosphineoxide(TOPO)

In order to study the synergistic effect, the other extractant used along with TOPO for study of extraction of cobalt is TOA.

The chemical compound TOA belongs to the aliphatic amines and tertiary amines groups. Tri-n-octyl amine has the chemical formula $C_{24}H_{51}N$ and a molecular weight of 353.67g/mol. It has a -34°C melting point, a 164°C boiling point, and a density of 0.810 g/mL. It's an anion exchanger in liquid form. It dissolves in low polarity solvents such as chloroform and toluene. In water, it is immiscible.

2.6 STRUCTURE OF TOA



Tri-n-octyl amine(TOA)

CHAPTER-3

REVIEW OF LITERATURES

REVIEW OF LITERATURES

3.1 SOLVENT EXTRACTION, A SHORT REVIEW:

Many experimental work has been carried out in the field of solvent extraction.It is a well-established technique in the hydrometallurgical process for removing and separating distinct metal ions after leaching and producing pure metal solutions for electrowinning. The above technique has been effectively used for extracting heavy metals.

A survey of literature is presented below:

Recovery Co(II) using polyetheleneglycol and its derivatives was carried out by Sotobayashi. [32]. In liquid-liquid extraction, polyethyleneglycol and its derivatives were discovered to be used as new extracting reagents for trace quantities of Co(II). The behaviourof Co(II) extraction from thiocyanate solutions using polyethyleneglycolalkylphenyl ether (Triton X-100) was investigated.

Hydroxamic acids are used to recover cobalt from solvents was carried out by Monzyk *et al.*[33]. Solvent extraction techniques are used to reversibly extract cobalt from cobalt-bearing aqueous solutions by contacting the aqueous solution with a hydrocarbon solvent containing a N-alkylakanohydroxamic acid with at least 8 carbon atoms. In addition, a new class of cobalt compounds is described.

Liquid-liquid extraction of Co(II) ions was done by Rafigi .[34]. The extractive characteristics of HL1, 2-hydroxy-1-naphthaldoxime and HL2, 1-hydroxy-2-naphthaldoxime towards cobalt(II) ions have been investigated. The shifting of extraction % curves towards a lower pH region indicates a synergistic effect of these.

Tri-octylamine and neutral donors work together to extract cobalt(II) in a synergistic way was studied by Biswas *et al.*[35]. This paper describes a study that used a combination of trioctylamine (TOA) and neutral organophosphorous donors to extract cobalt(II) spiked with 60Co from hydrochloric acid solutions in carbon tetrachloride. Distribution data were used to calculate synergistic coefficients and adduct formation constants, which were then connected with the basic character of donors.

Co(II)/Ni(II) extraction and separation using TIOA/TOPO was reported by Okatan *et al*.[36] and synergestics effect has been studied.The effects of several parameters on cobalt extraction and stripping were explored, and the best synergistic extraction and stripping conditions were discovered. To assess the synergism between TIOA and TOPO, the extraction of cobalt was studied under optimal circumstances.

Using the Cyanex 272 for extracting and separating Co(II) from CH3COONA medium was Carried out by Nikam [37]. Cyanex 272 as an extractant with toluene established a simple solvent extraction technique for appreciable extraction of Co(II) from sodium acetate (0.5M) solution. The extraction and stripping characteristics of these metals have been used to separate cobalt(II) from various binary and multicomponent combinations. The

method was improved to separate and determine cobalt(II) from real-world materials. The results of the approach are compared to the results of other methods to ensure the method's reliability.

Hydrometallurgical Recovery of Co(II) was studied by Zuzanna *et al.*[38]. The study focused at separation of Co(II) from spent industrial catalyst which was followed by leaching of wastage catalyst in the above method. From the result it is concluded that the proposed approach can favour Mo(VI) and Co(II) from the spent catalyst, eliminating Fe(III) Al(III).

Tri-n-efficacy octylamine's in extracting Co(II) from an acidic chloride medium via water-liquid extraction Efficiency of tri-n-octylamine for the water-liquid recovery of Cobalt(II) was studied by Mishra *et al.*[39]. Cobalt criticality is rising over time, prompting researchers to seek out efficient cobalt recovery strategies. The extraction of cobalt from acidic chloride medium using tri-n-octylamine (TOA) in kerosene is described in this work. Using 1.5 M TOA, the extraction percentage was found to be 76.7. The effects of several salting out agents such as NH4Cl, KCl, and NaCl on percentage extraction have been studied, with KCl emerging as the most advantageous. The positive enthalpy change value shows that high temperatures favour the development of extractable complexes (Co (II)-TOA complexes), andthe positive entropy change value suggests inner sphere complexation. Under the current experimental conditions, kerosene as a diluent was found to be more effective than other aromatic hydrocarbons in extracting Co. An FTIR analysis was performed to investigate the interaction between cobalt and TOA. The position of functional groups' absorption peaks changed, indicating that TOA binds to Co. (II).

Liquid-phase microextraction of Co ions was carried out byTorabi *et al*.[40]. Extraction of cobalt ions, a new DES of n-phenyliminodiacetic acid: choline chloride (2:1 mol ratio) was developed, which serves as both a chelating agent and an extraction solvent. Limits of detection and quantification of 5.23 g L1 and 17.67 g L1, respectively, were attained under ideal circumstances. It was introduced for spectrophotometry assesment of Co in traces.

Slug Flow Separation and Recovery of Li, Co, and Ni in an Aqueous Phase was studied by Mikiya *et al*.[41]. Slug flow extraction provides a higher mass transfer rate and faster phase separation than conventional extraction. As a result, there are numerous benefits, such as the device's volume shrinking and the solvent being considerably decreased. In this work, lithium, cobalt, and nickel ions were separated via slug flow extraction. Each segment of the liquid's circulation flow strength, as well as its volume flow ratio, affect the overall picture's mass transfer volumetric coefficient.

Recovery Co(II) by solvent extraction was carried out by Gupta [42]. Cobalt (II) is separated from hexaacetatocalix(6)arene in toluene using a novel solvent extraction procedure. Hexaacetatocalix-6-arene was used to recover Co(II) at pH 7.4 followed by stripping in nitric acid (2M) .

Cobalt extraction using a proprietary alkylated 8-quinolinol was carried out by Flett *et al.*[43]. To generate a complex of Co(III), a KELEX 100 demonstration was conducted. when cobalt (Co(II)) is extracted.

Bis(2,4,4 trimethylpentylphosphinic acid is used as an extractant for separation cobalt and nickel by Rickelton *et al.*[44]. Researchers looked into the use of an organophosphinic acid in solvent extraction as well as calcium rejection, according to comparative data. These include limited solubility in water and hydrolytic stability of the reactants, among others. Cobalt may be recovered from concentrated nickel sulphate solutions using a counter-current, mini-plant, continuous test.

Solvent extraction of Ni, Co, Cu from asulphideconcentrate leach liquid was carried out by Sahu[45]. As part of UCIL, Uraium Corporation of India Limited copper concentrate processing, Liquid-liquid extraction was used to recover important metals. LIX 84 in kerosene was used to recover copper from the leach liquid. Co and Ni were extracted using sodium salt Cyanex 272.

Cobalt (II) extraction from HCL solutions in Alamine 336 and meta-xylene systems was reported by Sayar *et al.*[46]. 1, 3 and 6 g L1 of metal concentration were used in the extraction trials, with HCl concentrations of 1, 5, 8 and 10 M, respectively. The recovery of Co(II) rises with increase in acid conc. , according to the research. To obtain Co(II) at concentrations of 5 to 10 M, Alamine 336 was extremely soluble in m-xylene. The extractability of metal & volume content of Alamine 336 were correlated using a mathematical model. The optimal Alamine 336 content for one stage extraction was determined.

Various solvent extraction steps for refining cobalt solutions: MEXTRAL and D2EHPA were used as extractants was studied by Mulaja *et al*.[47]. In order to remove copper (1.35 g/L Cu2+) and a zinc-iron-manganese complex in two phases, MEXTRAL and D2EHPA were used. Various properties were studied to determine their effects. Taguchi's L16 (44) experiment optimised these four parameters to increase the purification extent. Succeeding extractions showed that the Cu, Fe, Zn and Mn contents were reduced by 98.7, 97.6, 98.7, and 80.4 percent, respectively. This work demonstrated the ability of getting high purity cobalt , which now account for 49 percent of its global use. According to estimates, cobalt has a coextraction value of 6.2%.

Separation of Cobalt(II) from Industrial Effluent using a Diffusion Dialysis and Extraction Integrated System was studied by Aleksandra *et al*.[48].In this paper, we describe a multistage hydrometallurgical extraction of Co(II) from wastewater using diffusion dialysis (DD) to reduce the acidity of industrial effluent – pregnant leach solution (PLS), followed by precipitation of Al(III), Fe(III), and CrIII hydroxides, and selective extraction of Co(II) with bis(2,4,4-trimethylpentylphosphinic acid (Cyanex 272). By using a low flow rate but for a longer time, the DD findings show that it is possible to produce the lowest amount of metal ions in the dialysate and a high H+ concentration (1,5 to 3 M). Cr(III), Al(III) hydroxides, as well as certain admixtures of Cu (II) and Fe(III) were successfully removed from the feed following DD, allowing the water-liquid extraction of Co(II) at pH 5.4 to proceed. Due to high distribution ratios, the ions of Co(II) is considerably isolated from other ions in the feed, such as Ni(II), and delivered to the organic phase of the feedstock. Dialysate is more efficient at removing metal ions from extracts than H2SO4 solution, resulting in a Co(II) rich electrolyte.

TOA was used to extract Co(II) from a nitrate solution using liquid water. was studied by Mohanty *et al*.[49]. There are many commercial uses for cobalt, but if there is too much of it, it can have a number of harmful repercussions. Chemical contaminants can be removed from the environment using the liquid-liquid extraction process. Researchers studied the effects of nitric acid concentration, equilibration period, extractant concentration and cobalt ions on cobalt extraction in toluene. The extraction equilibrium took 15 minutes to reach. With 0.1 M TOA, 99 percent of the cobalt was extracted. The cobalt loading increased as metal ion concentrations increased. When it came to the extraction process, the presence of nitrate ions had almost no effect. With different stripping agents, 99.15 percent back extraction was achieved with 0.1 mol/L $(NH_4)_2CO_3$ in the organic phase. The FTIR and slope measurements were used to develop the extraction method.

Ionic liquid extraction of cobalt and lithium from spent lithium-ion battery leach liquors using Cyphos IL-101 was studied by Lei Xu *et al*.[50].Inevitably, lithium-ion batteries will degrade and eventually be scrapped, creating a massive urban mine of dead batteries. Using subsequent & hydrometallurgy recover techniques, precious metal ions can be extracted from these batteries. For the extraction and recovery of lithium cobaltoxide (LiCoO2) battery leach liquors, Cyphos IL-101 has been proposed. With outstanding stability and high extraction capacity (35.25 g/L),Cyphos IL-101 effectively removed Co ions. The Co and Li separation factor (Co/Li) in HCl at 60°C with 0.5 M was 102.11. The leach liquors from spent Li-ion batteries also exhibited an increase in Co extraction with an increase in temperature UV–Vis absorption spectra, Fourier transforms, and Fourier transforms were used to characterise the extractants before and after application. 87.4 percent and 74.2 percent of cobalt and lithium were recovered by precipitation after extraction separation

using Cyphos Il-101. 90.5 percent of Co and 86.2 percent of Li were recovered by precipitation after extraction separation using cobalt oxalate and lithium carbonate with the purity of 87.4 percent and 74.2 percent, respectively. For the recycling of lithium cobalt oxidebatteries, this approach could be a potential option.

Cyanex 301 extracts cobalt and nickel from sulphate solutions simultaneously in the presence of manganese and magnesium. was carried out by Tsakiridis *et al.*[51]. This was done with Cyanex 301, a thio-organophosphinicextractant diluted in Exxsol D-80. Statistical design and analysis of trials were used to establish the key impacts and interactions of the solvent extraction parameters, which included the extraction pH at equilibrium, temperature, extractant concentration, and organic to aqueous phase ratio. In order to determine the nature of the cobalt and nickel complexes extracted, a slope analysis method was applied. Cobalt and nickel extraction and stripping methods were also examined in terms of the number of stages required.

Cyanex 272 solvent extraction separation of cobalt (II) from nickel and other metals was carried out by Gandhi *et al.*[52]. To extract cobalt at pH 8.0 using chloroform, five times as much Cyanex 272 [bis(2,4,4-trimethylpentyl)phosphoric acid] was utilised. The cobalt (II) was extracted using nitric acid, and the combination with the nitroso R salt was determined using spectrophotometry. Cobalt was used to extract vanadium, chromium, nickel, manganese, iron, and zinc (II). Mixtures with varying amounts of iron, cobalt, and nickel can be separated using the proposed approach.

Solvents are used to extract Co(II) from sulphate solutions with cobalt extractants was carried out by Wiegers *et al.* [53]. Scaling of equipment and cobalt recycle are reduced by controlling aqueous pH at the extraction, cleaning, and stripping stages to maximise cobalt loading and selectivity, while scale-causing ions such as calcium, nickel, and cobalt are recovered separately using a cobalt-selective organic extractant.

Cyanex 302 is used to extract cobalt(II). was carried out by Menoyo *et al.* [54]. Using Cyanex 302 [bis(2,4,4-trimethylpentyl)monothio-phosphinic acid] diluted in toluene, the extraction equilibrium of cobalt (II) from 1.0M potassium chloride has been examined. There have been studies on the impact of pH, extractant concentration, and metal concentration on extraction behaviour. Cobalt extraction has also been studied in relation to bis(2,4,4 trimethylpentyl) dithiophosphinic acid, one of the minor impurities in Cyanex 302 as well as the primary component in Cyanex 301. LETAGROP-DISTR was used to visualise and analyse the experimental data. The results can be explained by assuming the extraction of species $CoR_2(HR)$, $CoR_2(HR)_2$, CoL_2 and CoCIL(HL), where HL is bis(2,4,4-trisphosphate).

Separation of cobalt and nickel utilising acidic organophosphorus compounds as a solvent. was carried out by Komasawa *et al.*[55]. When di-(3-ethylhexyl)phosphoric acid (HDEHP) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester are used to extract cobalt and nickel from an aqueous solution containing both metals, an interaction occurs (EHPNA). For ideal conditions where only monomeric metal species are extracted, an extraction equilibrium expression for a mixed metal species has been constructed as a function of the amounts of cobalt and nickel and the extraction constants involved. With the

exception of a highly loaded organic phase, the presented results are found to be comparable to those obtained utilising pure metal extraction data.

Cobalt (II) extraction using hydroxynaphthaldoxime and neutral donors in a synergistic manner was studied by Banerjee *et al.*[56]. Cobalt II has been extracted from hydrochloric acid aqueous solution utilising the oxime derivative of -hydroxy naphthaldehyde in o-xylene, according to reports. We synthesised and analysed the ligand in our lab. The usual pH range for extraction of Co (II) by the ligand-donor combination was found to be between 8 and 9. Various donors, such as dimethyl sulphoxide (DMSO), trioctyl phosphine oxide (TOPO), and bis(2ethylhexyl) phosphonate, as well as diluents, were thoroughly investigated for their impacts on Co(II) extraction utilising the current method. In the organic phase, the binary adduct formation constant (log kex) was found to be 3.182. The ternary species [CoA](DMSO)(Cl), "CoA" (TOPO), and "CoA" (phosphonate)(Cl) were found to have log K values of 6.42, 6.22, and 6.25, respectively. The equilibrium constants trended in the same direction as their basic character (DMSO TOPO Phosphonate). The data was extrapolated to determine the amount of Cobalt in medical drugs and cobalt-containing ore samples.

Flotation of Co(II) ions and precipitates in the presence of decanoic acid and liquid-liquid extraction was studied by Beheir *et al*.[57]. We perform ion and precipitate flotation of Co(II) from chloride medium with a starting concentration of 1:10-4M Co(II) and/or z=0. The results were compared when decanoic acid was added. In the fiquid-liquid extraction, hydrogen peroxide (CH_2O) was used, while ethanol was used in the flotation. During liquid-liquid

extraction, $(CoR_2)_2(HR)_2$ is generated, however flotation occurs due to the formation of a surface active product (CoR_2), having empirical formula CoR_2. On the three separation processes, the effects of pH and decanoic acid concentration were investigated.

Recovery of Cobalt(II) and Nickel(II) through liquid-liquid extraction with chlorendic acid was studied by Berger *et al*.[58]. In this studies, a hexachlorosubstitutednorbornyl 1,2-dicarboxylic acid, was used to extract Fe(III) 1 and Cu(II) 2. These ions can be eliminated with greater than 90% effectiveness in the pH ranges of 1-3 and 3-5. As a result, the extraction properties of Nickel II (Ni II) and Copper II (Co II), as well as different monocarboxylic acid extractants, are compared.

CHAPTER-4

EXTRACTION OF Co(II) USING TOPO AND TOA

EXTRACTION OF Co(II) USING TOPO AND TOA

4.1 EXPERIMENTAL: (LIQUID-LIQUID EXTRACTION CARRIED OUT IN OUR LABORATORY)

4.1.1 SOLUTIONS AND REAGENTS

SYSTEM 1:

Mohanty A *et al*.[59] extracted Co(II) using TOA(Tri-n-octyl amine) in toluene. The stock solution of Co(II) (0.01M) was prepared. Without further purification, Sigma-sample Aldrich's of TOA was used. Toluene was used as a diluent in this experiment. Forthe TOA (0.05M) stock solution, the extractant was weighed and diluted in toluene. It was necessary to dilute both the aqueous and organic stocks in order to prepare aqueous (0.0005M) and organic (0.005M) working solutions, respectively. Everything else that was used was of a high analytical grade.

SYSTEM 2:

Dash A *et al*.[60] has extracted Co(II) using the extractant TOPO (Tri-n-octylphosphine-oxide). Heavy Metals, Talcher provided a sample of TOPO that was used without further purification. Toluene was used as a diluent in this experiment. Weighing the desired amount of extractant and diluting it in toluene resulted in a 0.05M stock solution of TOPO. It was necessary to dilute both the aqueous and organic stocks in order to prepare aqueous (0.0005M) and organic (0.005M) working solutions, respectively. Everything else that was used was of a highanalytical grade.

SYSTEM 3:

As Rauta N *et al*.[61] has shown, the mixture of TOPO and TOA can be used to extract Co(II). After dissolving the required amount of cobalt nitrate,$Co(NO_3)_2$, in double-distilled water, the stock solution of Co(II) (0.01 M) was prepared for use. No purification was performed on the samples of Heavy Metals, Talcher and Sigma-TOA Aldrich's and TOPO. Toluene was used as a diluent in this experiment. For the TOPO (0.05 M) and TOA (0.05 M) stock solutions, the extractants were weighed and diluted in toluene. Aqueous (0.0005M) and organic mixture (0.0025M TOPO + 0.0025M TOA) working solutions were resulted by diluting the aqueous as well as organic stocks according to the requirements. Everything else that was used was of a high analytical grade.

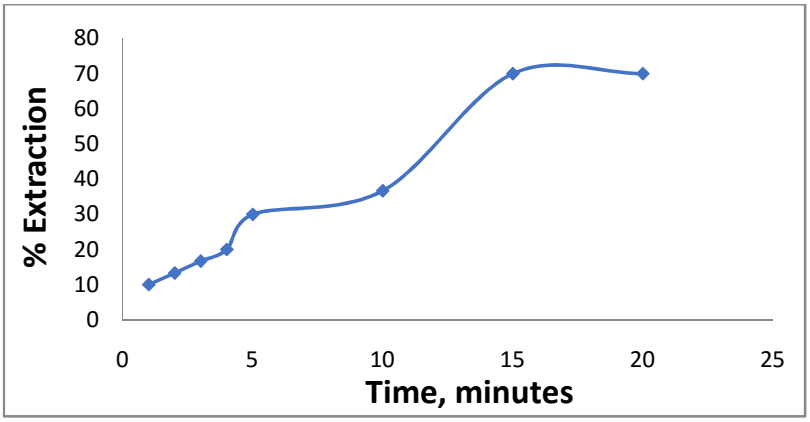
4.1.2 EXPERIMENTAL METHODS

We carried out extraction experiments with equal portions of the aqueous and organic phases, shaken for 15 minutes with mechanical shakers. The conc. of metal was determined using colour developing reagents (KSCN, N/2 HCl, and acetone) at a wavelength of 585 nanometers (nm) using a UV visible spectrophotometer as soon as the phases separated (SYSTRONICS 105). It was feasible to calculate how much metal ion was in the organic phase using the difference in metal ion concentration in the aqueous phase before and after extraction. All of the experiments were to be carried out at room temperature.

4.2 RESULTS AND DISCUSSION

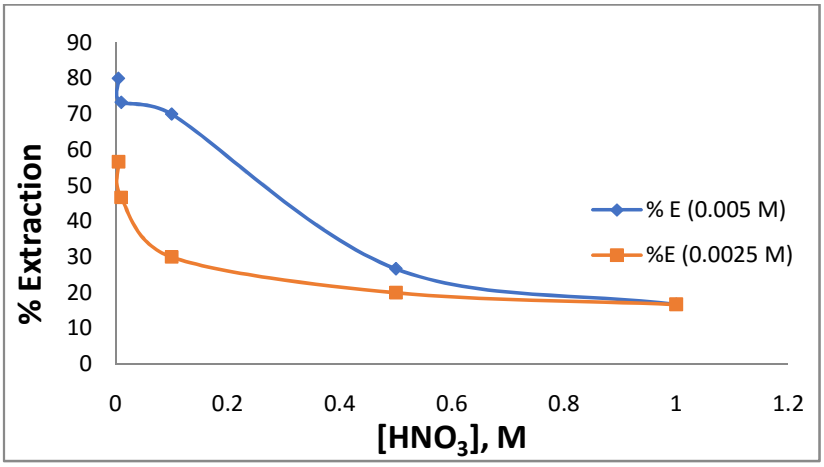
SYSTEM 1:

- **Effect of equilibration time**



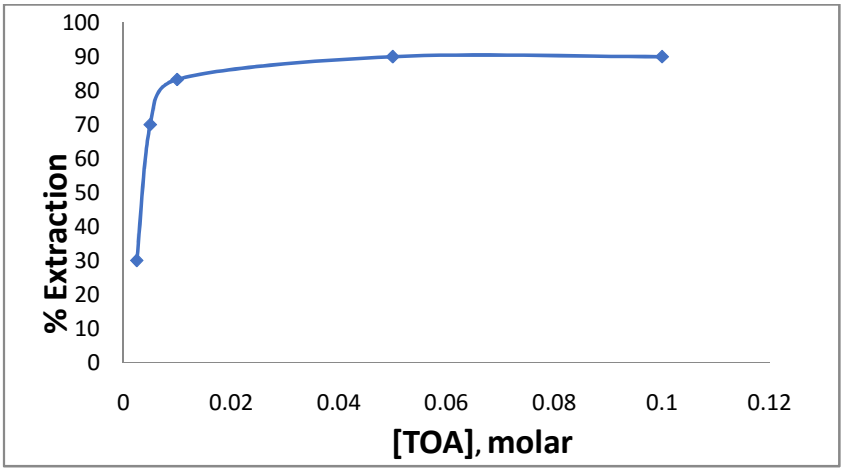
(Figure 1)

- **Effect of nitric acid concentration**



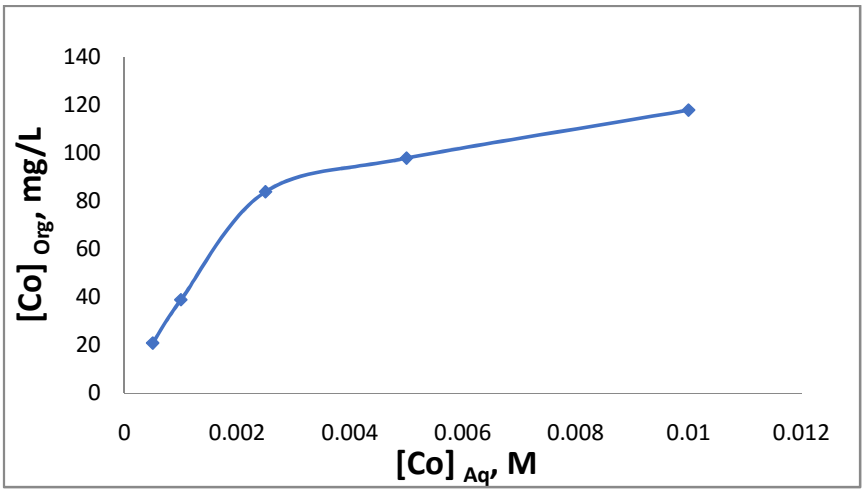
(Figure 2)

- **Effect of extractant concentration**



(Figure 3)

- **Effect of concentration of aqueous phase**



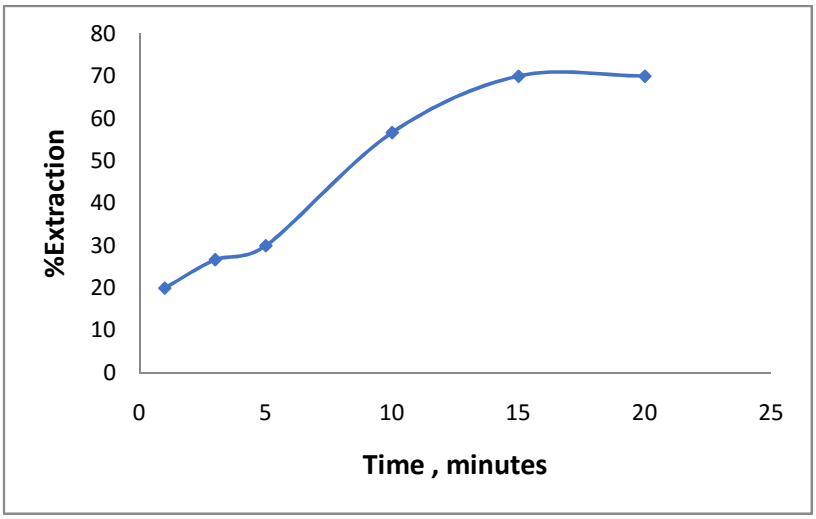
(Figure 4)

4.2.1 RESULTS :

- Equilibration time was reached at 15 minutes.
- At acid concentration 0.005M(HNO_3),the percentage recovery of Co(II) was 80% and 56.66% with extractant concentrations 0.005M and 0.0025M respectively.
- Extraction % varied from 30% to 90% with increase in conc. of extractant from 0.0025M to. 0.001M.
- Extraction % varied from 70% to 20% with increase in conc. of aqueous layer from 0.0005M to 0.01M.

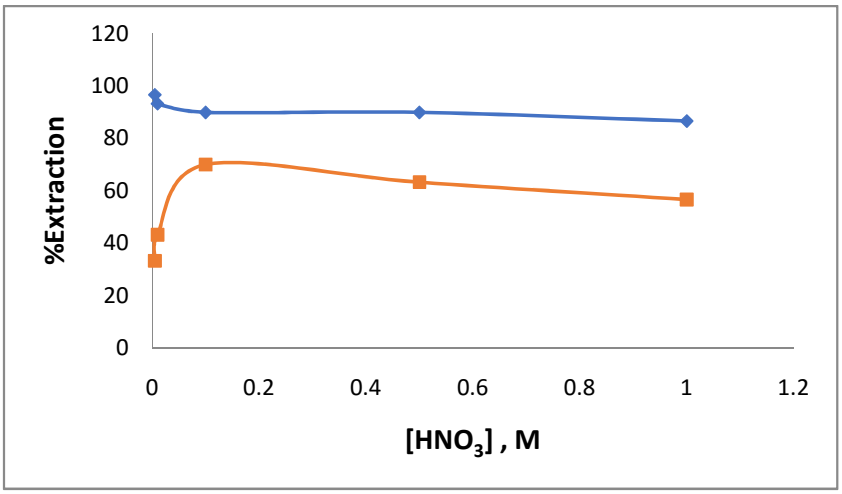
SYSTEM 2:

- **Effect of equilibration time**



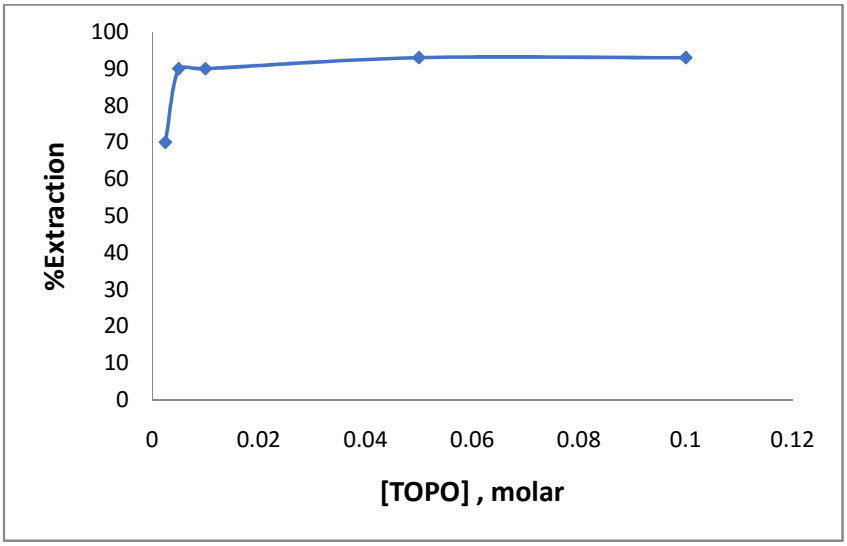
(Figure 5)

- **Effect of nitric acid concentration**



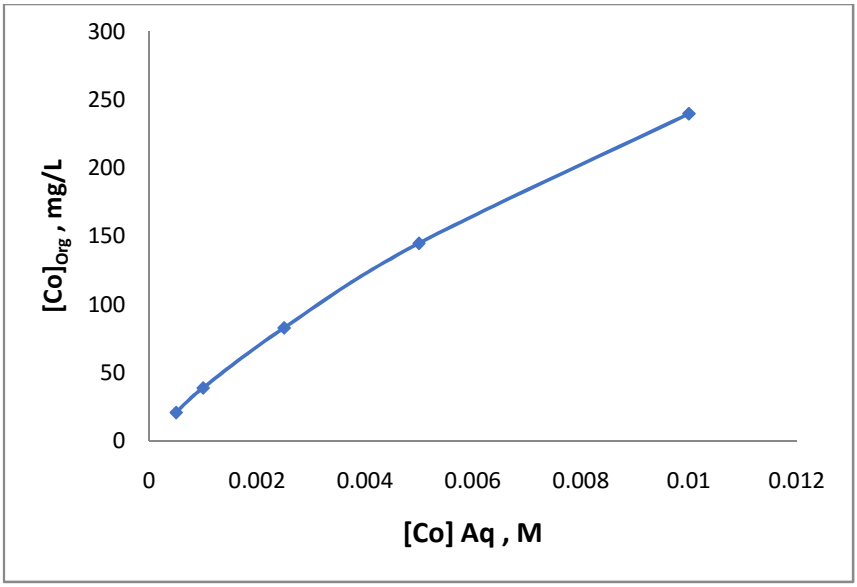
(Figure 6)

- **Effect of extractant concentration**



(Figure 7)

- **Effect of concentration of aqueous phase**



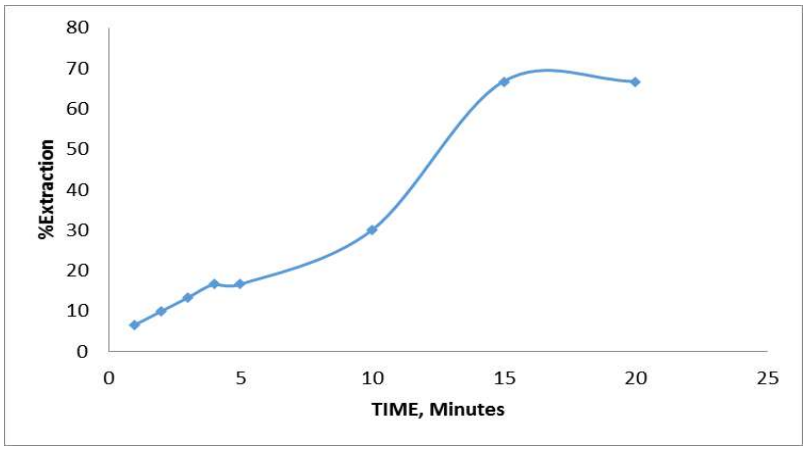
(Figure 8)

4.2.2 RESULTS :

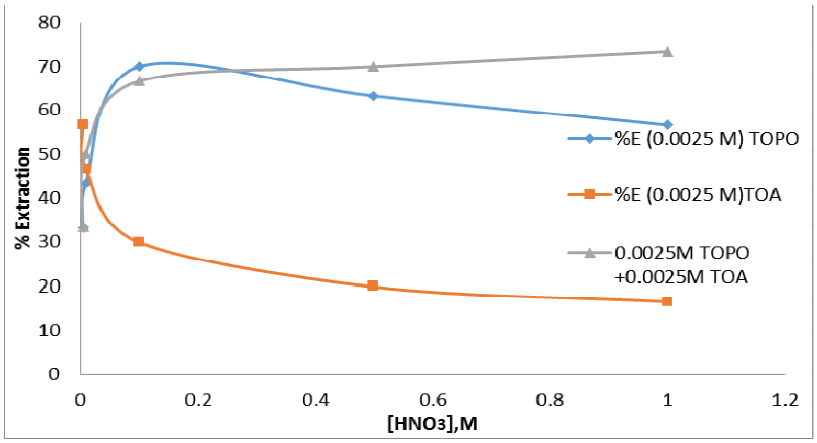
- Equilibration time was reached at 15 minutes.
- At acid concentration 0.005M(HNO_3),the percentage recovery of Co(II) varied from 96.66% to 33.33% .
- % Extraction of Co(II) varied from 70% to 90% with rise in conc. of extractant from 0.0025M to. 0.001M.
- % Extraction of Co(II) varied from 70% to 40.66% with rise in conc. of aqueous phase from 0.0005M to 0.01M.

SYSTEM 3:

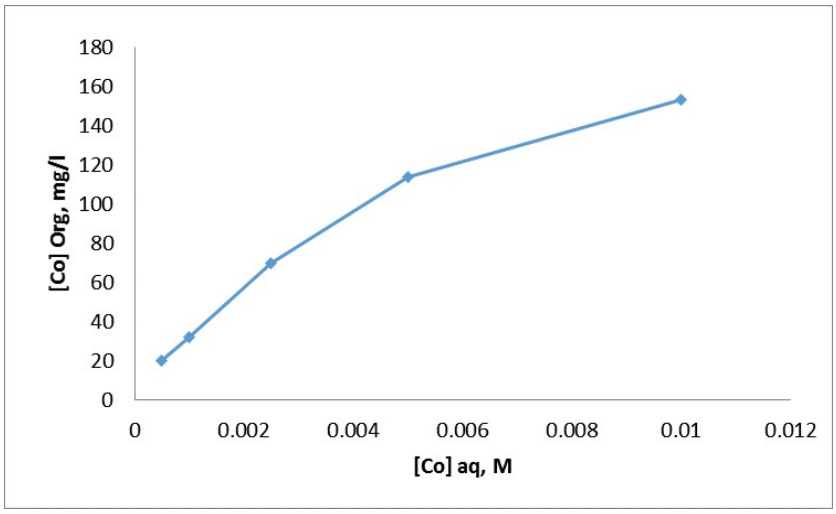
- **Effect of equilibration time**



(Figure 9)



(Figure 10)


180
160
140
120
100
80
60
40
20
0
[Co] Org, mg/l
0
0.002
0.004
0.006
0.008
0.01
0.012
[Co] aq, M

(Figure 11)

4.2.3 RESULTS :

- Equilibration time was reached at 15 minutes.
- Extraction % of Co(II) using 0.0025M TOPO increased from 33.33% at acid concentration 0.005M to 70% at acid concentration 0.1M and then decreased to 56.66% at acid concentration of 1 M. The % recovery of Co(II) using 0.0025 M TOA was 56.66% at conc. of acid 0.005 M and decreased to 16.66% at 1 M.
- Extraction % of Co(II) using 0.0025 M TOPO and 0.0025 M TOA increased from 33.33% at acid concentration 0.005M to 73.34% . The % recovery of Co(II) using mixture of 0.0025 M TOPO and 0.0025 M TOA decreased from 66.67% to 25.93% with increase in concentration of the aqueous solution from 0.0005 M to 0.001M.

CHAPTER-5

CONCLUSION

CONCLUSION

Literature has been surveyed from which it is observed that cobalt has been effectively extracted using various extractants namely TOPO , TOA , Polyethylene glycol ,Hydroxamicacid,Cyanex 272, β hydroxynaphthaldoxime , Decanoicacid,Chlorendic acid etc, by the method of liquid-liquid extraction in the last decade. Effect of equilibration time, acid concentration , extractant concentration, concentration of aqueous phase have been studied and co-related with the extraction efficiency of the extractant. List of efficient extractants is given below:-

- According to Mohanty A et al. 99% of Co(II) was extracted from nitrate solution using liquid-liquid extraction.
- By Dash A et al. percentage of cobalt extraction was 96% using TOPO.
- By Rauta N et al. cobalt extraction percentage of 70% using mixture of TOPO and TOA.
- By Berger et al. percentage of cobalt extraction was 90%.
- By using the hydroxynaphthaldoxime and neutral donors, Banerjee and his colleagues were able to extract Co(II) at an extraction rate of 80 %.
- Michael Mikiya et al. have studied the slug flow method for lithium, nickel, and cobalt extraction, and found that the recovery rate of extracted ions is 90-95%.

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