LIQUID-LIQUID EXTRACTION OF Cr(VI) FROM AQUEOUS SOLUTION: A SHORT REVIEW

By

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A

THESIS SUBMITTED TO

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MASTER OF SCIENCE IN CHEMISTRY

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CERTIFICATE I

This is to certify that the thesis entitled **"Liquid-Liquid Extraction of Cr(VI) 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 **POOJA JENA** 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: Bhubaneswar **CHAIRMAN**

Date: **ADVISORY COMMITTEE**

CERTIFICATE II

This is to certify that the thesis entitled "**Liquid-Liquid Extraction of Cr(VI) from Aqueous solution: A Short Review**" submitted by **POOJA JENA** 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

The metallic pollutants play a vital role in environmental pollution as metals are nonbiodegradable. There are numerous applications for chrome in human beings and industries, making it a highly sought-after metal. It is extremely hazardous and should not be used. Waste water must be purified before it can be discharged into surface waters. The chemical reduction of Cr (VI) is expensive and produces secondary pollutants as well. Water-liquid extraction is a popularly adopted technique in the process of hydromettalurgy for the removal and separation of various metal ions after leaching and is capable of producing pure metal solutions that are used in electrowinning processes. It is therefore possible to use this process to clean the environment of harmful chemicals. For example, TOPO, TBP, and cyanex272 are organic extractants that are widely used. The current study describes the extraction of hexavalent chromium by the method of solvent extraction done by researchers using different extractants and the co-relation of different parameters with extraction efficiency of the extractants, used. Chromium has a wide range of applications because it is used to harden steel, manufacture stainless steel, and create a variety of alloys. Steel can be given a polished mirror finish with chromium plating. Chromium compounds are also used in the manufacturing of industrial catalysts and pigments.

ACKNOWLEDGEMENT

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Finally, I prostrate myself before the Almighty, whose omnipresence has always guided and assisted me in overcoming all adversity.

Place :

Date : **(POOJA JENA)**

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CHAPTER-1

INTRODUCTION

INTRODUCTION

Nowadays Active industrialization plays a key role in the rise of industrial waste in water resources, which includes gross toxic metals in it. As a result, removing these toxic metals from industrial waste water is a top priority. [1]

Metal-containing hazardous industrial waste must be treated before being discharged. Adsorption, electrochemical deposition, ion exchange, Co-precipitation, membrane filtration, solid phase extraction, and liquid-liquid extraction etc. are some of the techniques used to treat them.

It is a well-known method for removing and separating metal ions after leaching and producing pure metal solutions for electrowinning [2,3]. It is economically favourable. It is an extremely creative, low-cost, and quick method. Because of its effectiveness it is widely used.

The method is used exclusively in the recovery and purification of dissolved heavy elements such as Cr, Co etc. and other rare earth elements in industrial belt water from a hydrometallurgical standpoint.

Chromium is released from various industries such as electroplating, tanning, wood preservation, metallurgy, and textile synthesis. It is one of the popularly distributed heavy metals in the Environment. Various industries discharge large amounts of Cr-containing waste water and sludge, causing environmental issues.

Chromium is a highly valued element which is naturally found in rocks, river belts, gases and soils.It enhances protein, carbohydrate, and lipid metabolism and improves insulin sensitivity. It can be found in a variety of o.s in which trivalent and hexavalent chromium are the most stable forms or common valence states, though their biological and toxicological properties differ significantly.

According to Marsh et al. [4], the maximum amount of total chromium allowed in drinking water is 0.05 mg/L. (WHO 2004). Ouejhani et al. [5] found that liquid-liquid extraction with tributylphosphate can effectively recover hexavalent chromium from acidic chloride media.

An attempt has been made in this study to throw light on the recovery of chromium which can be recycled for various other applications. Chromium is used to harden steel, make stainless steel, and make a variety of alloys. Steel can be polished to a mirror finish with chromium plating. Industrial catalysts and pigments contain chromium compounds.

CHAPTER-2

THEORETICAL BACKGROUND

THEORETICAL BACKGROUND

2.1 LIQUID-LIQUID EXTRACTION

It is an interphase transport process that studies the distribution of a chemical substance between two phases by keeping two immiscible liquids in contact. A substance's distribution is determined by its solubilities and phase volume ratio. In the analytical separation method, this technique is used. It has been used to separate metals in solution that are similar in nature, as well as to purify the mixture for getting products with purity. At both macro and tracer concentration levels, it helps in easy recovery of materials. Solvent extraction is also referred to as liquid-liquid extraction. One is the organic layer, which contains the extractant and sometimes diluents, and the other is the aqueous layer, which contains the metal ion in a biphasic liquid system. Diluent is used to reduce the extractant's viscosity and improve its extraction ability. In some industrial applications, a component known as a modifier is add to inhibit the third phase formation. A continuous and multistage extraction system is used to recover nuclear materials quantitatively. Peligotet al.[10] published the first research paper on liquid-liquid extraction of uranyl nitrate using diethyl ether as a solvent in 1842. Several researchers have examined the principles, applications, and scope of liquid-liquid extraction techniques. Morisson and colleagues [11], Marcus 12], De et al.[13], Sekine et al.[14], Ritcey.[15], Rydberg l.[16], Sahu.[17], Rice[18], Shmidt et al.

2.2 PRINCIPLES OF LIQUID-LIQUID EXTRACTION

Distribution law

The Nernst partition isotherm[30] governs the distribution of a solute. According to this law, at equilibrium, the distribution ratio, also known as the partition coefficient, is equal to

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

In a higher concentration solution, eq.(2.1) becomes,

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

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

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

Mathematically it is defined as,

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

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

Based on how the system interacts with its components, the kinetics of an extraction system differs.

2.3 EXTRACTANTS AND THEIR CLASSIFICATIONS

Ideally, commercial extractants should have the following characteristics:

1)high molecular mass

2)Low solubility in aqueous solution

3)High-capacity loading of metal

4)Large range of solubilities in both non-acidic and acidic solvents

5)non-flammable, non-volatile &non-harmful.

They are divided into three categories: chelating, liquid ion-exchangers and solvents.

Chelating extractants

A metal ion's coordination requirement is met by coordination, which helps to neutralise the metal's charge. A lack of charge neutralisation results in water molecules occupying vacant coordination sites, making the complex more hydrophilic and reducing extraction. Basic chelating agents are bidentates, which form cyclic compounds in most cases. There is a preference for five- or six-membered rings because for their thermodynamic stability. The coordination atoms include oxygen, nitrogen, and sulphur.

Chelating extractants include LIX, SME, Acorga, and Kelex. It is common to use -diketones for actinide extraction, such as pyrazolines and iso-oxazolines.

Liquid-ion-exchangers

As a general rule, liquid cation exchangers and liquid anion exchangers fall into two categories.

(a) Liquid cation exchangers

As a result of their ability to donate proton, they are also known as acidic extractants.

They remove metal ions by performing the following chemical reactions:

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

To this group of compounds belong organophosphorus acids, monocarboxylic acids, and flurocarboxylicacids .

(b) Liquid anion exchangers

When it comes to anion exchangers, amines with high molecular weights are typically used. This is done by protonation before extracting the anionic metal species, which is then done by anion exchange.

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

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

As an example, Alamine 300,Alamine304 , and Alamine308 can be used as anion exchangers.

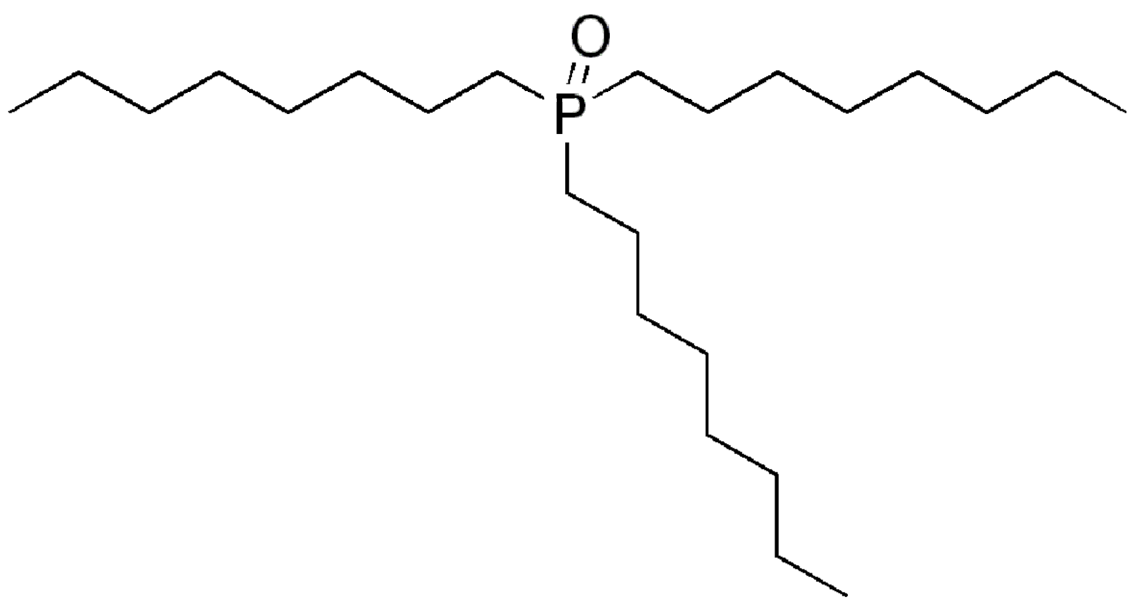
Solvating solvents

Inorganic solutions can be extracted with these ligands, which are neutral. In order to facilitate the extraction of metal complexes, water molecules are removed from the hydration sphere to make it more hydrophobic. This group of extractants includes ketones, alcohols, esters, ethers, etc. There are a number of organophosphorus extractants in this category, including TOPO, and TBP, among others, and long-chain dialkylsulphoxides. Recently, neutral extractants such as phosphine sulphides, CMPO, and phosphine oxides have been used as multifunctional organophosphorus extractants.

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

The extractant used for recovery of Cr(VI) in our laboratory is Tri-n-octylphosphine Oxide [(TOPO),OP($C_{18}H_{17}$)$_3$]. When used in the process of liquid-liquid extraction, tri-n-octylphosphine oxide is an effective solvating extractant. This compound can bind to metal ions because of its high polarity, which is caused by the dipolar phosphorus-oxygen bond. Low-polarity solvents such as kerosene, toluene, etc. are soluble in octyl groups [31]. It has a melting point of 50-54 degrees Celsius and a boiling point of 411.2 degrees Celsius at 760 millimetres of mercury.

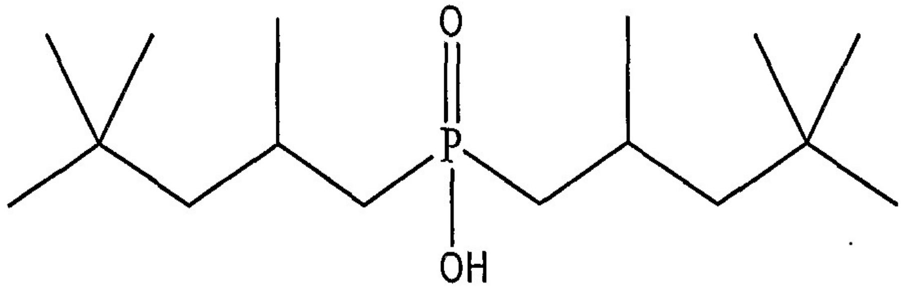
2.5 STRUCTURE OF TOPO



Tri-n-octylphosphineoxide(TOPO)

CYANEX272 was used with TOPO to study the synergistic effect. TOPO and CYANEX272 were used to extract Cr(VI).

2.6 STRUCTURE OF CYANEX272



CHAPTER-3

REVIEW OF LITERATURES

REVIEW OF LITERATURES

3.1 A REVIEW ON SOLVENT EXTRACTION

Experimental works have been carried out in the field of solvent extraction. To remove and separate various metal ions after leaching in hydrometallurgical processes, solvent extraction is widely used. It can produce pure metal solutions for electrowinning. Liquid-liquid extraction techniques have been used to extract heavy metals from the environment.

A survey of literature is presented below:

Chromium(VI) was also recovered by using TOPO was carried out by Ali kumbasar*et al*.[20] Using extractant TOPO, The recovery of chromium (VI) has also been demonstrated. In this research, the favourable conditions for hexavalent chromium extraction was determined. Additionally, the effects of metal ions and acid concentrations were also examined. A few minutes were required to recover all of the Cr(VI) ions.

Chromium (VI) Extraction using TOPO was carried out by Huang *et al.* [21]. The extraction equilibrium of chrome (VI) have also been studied fromSulfuric acid solutions in which TOPO used as extractant. It was published by the Society of Chemical Industry in 1998.The Rosenbrock Method was used to determine different Hexvalent Chromium complexes.

Hexavalent Chromium Extraction using TOPO was carried out by White *et al.* [22]. In this chromium is extracted from the acidic solution of metal alkali salts.It was concluded by White and Ross (4) that dichromate can be recovered using TOPO hydrocarbon solutions. As a result sensitivity of the

Diphenylcarbazide method increases. It appeared that the chromium could be separated from solutions and it would invalidate the usual Diphenylcarbazide method.

Dispersive liquid–liquid microextraction of hexavalent chromium in water using a (deep eutectic) solvent was studied by M. Pourmohammada*et. al. [23]* It was studied that it was an eco-friendly and rapid method. BTEAC-phenol was used for the first time as a deliquescent DES solvent in hexavalent chromium's extraction. It is possible to prepare hydrophilic DES by using BTEAC as HBA. When it comes to complexation and microextraction, the presence of THF and the solution's Ph were found to be important factors. There are several advantages to the Proposed method which includes rapidity, well sensitivity etc. It is low in cost, and the recovery extraction rate for Cr(VI) is high. Because of its high accuracy and reproducibility, this method allows for the detection of light amounts of Cr(VI) in various water evidence. As a result of the developed methodology's green options, such as microextraction as its primary method, the use of environment friendly solvent is considered as favourable experimental method.

Selective and Simple extraction process for Cr(VI) in wastewater which was released from various industries was carried out by S.Kalidhasan*et al.*[24].Chrome (VI) has been extracted from its complex with tetrabutylammoniumiodide (TBAI). This method is relatively simple and environmental friendly. Isobutyl methylketone (MIBK) is used to extract the ion pair. Cr(VI) concentration in the organic phase was determined by spectrophotometry. The maximum wavelength is 366nm and the organic layer was characterised by FT-IR.. This research has examined the impact of several analytical parameters like pH, volume of aqueous layer, time of equilibration. To convert the toxic Cr(VI) into the non-toxic Cr(III) Ascorbic acid was used. In the chromium (VI) range of 0–2g mL1, the calibration graph was linear with a relative standard deviation of 2.4 percent. With the proposed method it was possible to detect 0.25 grammes of lead in 25 millilitres of aqueous phase. It was tested on waste water of electroplating industries, spiked water samples etc.

Cloud point extraction and optimization of chromium speciation in organic fertiliser as assistance for legislative aspects Ivero Pita de Sá *et. al*. outlined a procedure involving chromium speciation was developed. To determine Cr(VI) traces in the sample, alkaline extraction (USEPA 3060A) and cloud point extraction (CPE) are utilised. Temperature, sample mass, and extractor volume all had an impact on Cr(VI) extraction in organic fertilisers.

A Doehlert experimental design was utilised to optimise an alkaline extraction followed by CPE to determine Cr(VI) in the organic phase. As a result of the defined extraction conditions, most of the samples were free of humic compounds, resulting in accurate & precise results. As part of an LC-ICP-MS study, various extraction transactions were used to evaluate the possibility of Cr species interconversions. Cr(VI) in organic fertilisers can be determined using this method with no significant differences observed.

There were still some organic compounds that were affected by the high humic compound concentrations. This means that better extraction procedures must bedeveloped. Smaller samples can be used for analysis, which results in less interference while maintaining the same level of precision for Cr(VI) measurement. [25]

Chromium (VI) Extraction in Liquid using Tricapryl Methyl Ammonium Chloride The Application of Isoamylalcohol as a Diluent to Industrial Effluents was studied by Kalidhasan*et al.*[26].Chrome in industrial waste water was recovered and settled using a simple liquid-liquid extraction (LLE) method. The Cr(VI) is held by electrostatic attraction as an ion association complex of HCr,O-4- and extracted into the organic phase using isoamylalcohol (IAA) as the dilution agent. The extract was lucent, with no signs of a third phase forming in the extract. The effects of many experimental conditions that affect the extraction process have been thoroughly investigated. Using ascorbic acid as a reducing agent, it is possible to renew the organic phase containing the metal extractant. Fourier transform infrared was used to investigate the organic phases (FTIR). The method described above was used to extract chrome from synthetic effluents, genuine waste water samples, and a certified reference material.

In a sustainable emulsion liquid membrane process, chromium (VI) is reduced to chromium (III) using an extractive continuous extractor. NorulFatiha Mohamed Noah et al. describe a method based on a detailed analysis of Chromium (VI) reduction to Chromium (III) in a sustainable continuous emulsion liquid membrane process for the first time in their publication. The diluent is palm oil, the surfactant is Span 80, the extractant is trioctylmethylammonium chloride, and the internal reagent is acidic thiourea solution. Using ionic liquid extractants ([TOMA+][Cl640]) as wellas palm oil as a green diluent, a new method of extracting and recovering Cr has been developed (VI). According to the results, a favourable SCELM was constructed and optimised with 342rpm agitation, 170s retention duration, and a 1:15emulsion-to-feed ratio. Optimal process conditions for Chromium (III) recovery and enrichment were investigated. A 200 ppm external input appears to be the optimal range of conditions for recovering Cr from rinse electroplating wastewater. [27]

Solvent extraction is used to extract Cr(VI) from aqueous solution was studied by Mubeena*et al.*[28]. Anionic chromate extraction requires the use of a cationic carrier, such as HTAB in this study. As the chromium concentration increased, so did the extraction efficiency. A reverse extraction process can be used to re-extract Cr(VI) from the organic phase into 0.2 mol/L sodium nitrate. The effects of various stripping agents, HTAB concentration, pH, Cr(VI) concentration, equilibrium time, temperature, aqueous to organic phase ratio, and aqueous to organic phase ratio were investigated. With actual effluent, an acceptable result was obtained under ideal conditions .

Using trialkylamine/kerosene as a solvent, chromium(VI) was extracted from a hydrochloric acid solution was studied by Li *et al.*[29]. We investigated the extraction equilibrium of Cr (VI) with trialkylamine (N235, R3 N, R = C8–C10) using kerosene as a diluent. Systematically evaluating the strike of several analytical parameters such as pH, equilibrium time, and temperature Fourier transform infrared spectroscopy was used to determine the structure of organic solution (FTIR). The results showed that N235 in kerosene extracted 99.99 percent of the Cr(VI). As a result of using thermodynamic functions, we discovered that extraction was exothermic in nature. The organic solvent that had been loaded was regenerated using N_2H_4 + H_2SO_4. It is possible to re-use the chromium extraction solvent that was regenerated (VI).

Tricaprylamine Oxide Solvent Extraction Of Chromium (VI) From Aqueous Acid Solutions was studied by Hariharan [30]. The extraction of chromium has been studied (VI) with Tricaprylamine oxide (TCAO) in benzene have been conducted. Hydrochloric and hydrobromic acid extractions are nearly quantitative, while acetic acid extractions are partial. A number of variables, such as amine-oxide concentration, metal ions, acidity, and foreign ions, were studied to determine the optimal extraction conditions. The species that were extracted are then identified.

Chromium (VI) extraction from an industrial waste solution was studied by Agrawal *et al.*[31]. In order to remove Cr (VI) from chloride solutions, Cyanex 923 mixed with kerosene was used. Cyanex 923 and Cr(VI) concentrations in the initial aqueous feed, temperature and time of extraction, and the ratio of organic to aqueous phase (O/A) were all used to test the extractant's efficiency. The proportion of Cr(VI) extraction decreases as the temperature rises at various doses of Cyanex 923. As a result of the intervention, optimised conditions, only Zn interfered with Cr(VI). At an O/A of 2, 98.6-99.9% of the Cr(VI) was extracted in 3-5 minutes with an initial input concentration of 1g/L of Cr (VI). The organic phase produced following the removal of Cr (VI) was then washed with weak HCl solution to neutralise any NaOH trapped or attached to the solvent, followed by distilled water to remove any leftover NaOH residue. A subsequent extraction of chromium was carried out using the solvent that had been regenerated previously (VI).

Hexavalent chromium recovery from acidic chloride environments via liquid-liquid extraction with tributylphosphatewas studied by Ouejhani*et al.*[32]. Liquid-liquid extraction with tributylphosphate PO(C4H9O)3 is used to recover chromium(VI) from water samples (TBP). The best conditions for quantitative extraction of Cr were determined by varying experimental parameters such as shaking period, aqueous phase pH, hydrochloric acid concentration, hydrogen and chloride ion concentration, extractant concentration, and aqueous-to-organic phase ratio (VI). Based on log-log plots, the most likely species of hexavalent chromium in organic phase are $HCrO_3Cl$ and H_2CrO_4. Tributylphosphate was shown to be effective in eliminating chromium from acidic chloride medium (VI). This approach can be used to extract and determine chromium in both oxidation states [Cr(VI) and Cr(III)] in water samples due to the great selectivity of tributylphosphate (TBP) for chromium(VI).

Zinc is extracted from ammonium chloride solutions using sterically hindered ß-diketones and then mixed with tri-n-octylphosphine oxide in a solvent. was carried out by Weng Fu *et al.*[33]. The extraction of zinc from ammonium chloride solutions utilising a sterically hindered ß-diketone, 4-ethyl-1,3-octadione as the extractant has been examined when TOPO is present or missing. According to the findings of the study, the combination of XI-55 and TOPO exhibited synergistic effects on zinc extraction. The determination of the thermodynamic parameters H, S, and G in the XI-55 extraction system and XI-55-TOPO synergistic extraction system demonstrates exothermic zinc extraction. The total ammonia content has a considerable impact on the extraction constants and distribution ratios in both extraction systems. FT-IR experiments on zinc-loaded organic phases corroborated the non-extractability of zinc-amine complexes. A sterically hindered ß-diketone, 4-ethyl-1,3-octadione, was used as the extractant to extract zinc from ammonium chloride solutions.

Copper(II) extraction from sulphate medium in chloroform using Capric acid and tri-n-octylphosphine oxide in a synergistic manner was carried out by Adjel*et al.*[34]. Cu(II) extraction from 0.33 mol/dm3 Na_2SO_4 aqueous solution at 25°C in the absence and presence of tri-n-octylphosphine oxide was investigated using capric acid (HL) (TOPO). When capric acid is applied alone, the species CuL2(HL)2 is extracted. In the presence of TOPO, the extracted compound is CuL2(HL)2 (TOPO). The interplay of TOPO and HL affects the extraction efficiency significantly. The extraction constants have been determined and are now available for usage.

Uranium and lanthanides are extracted from phosphoric acid using a synergistic DOPPA-TOPO combination. was carried out by Krea*et al.*[35]. In this study, uranium and lanthanides were recovered from phosphoric acid. The degree of extraction has been demonstrated to be affected by many parameters such as H3PO4, SO42-, Fe(III), DOPPA, and TOPO concentration. Uranium and lanthanides have similar initial extraction rates, according to a kinetic study.

Organic acid extraction equilibrium with tri-n-octylphosphine oxide was carried out by Hano*et al.*[36]. The extraction equilibrium of organic acids with tri-n-phosphine oxide (TOPO) was determined. As a result, the salvation number for each acid molecule was the same as the carboxyl group number. The extraction equilibrium constant was influenced by the acid's hydrophobicity when hexane was used as a diluent.

Acidic organophosphorus extractants and their combinations with TOPO were used to extract zirconium and hafnium from hydrochloric acid solutions was carried out by Wang *et al.*[37]. At HCl concentrations ranging from 1 to 4 mol/dm3, single acidic organophosphorus extractants such as D2EHPA, PC88A, and Cyanex272 were able to extract Zr and Hf. The extraction % for both metals increased as the HCl concentration increased, however the dependency of separation factor on HCl concentration was the reverse in both extracatant systems. The mixes resulted in a Zr and Hf extraction that was synergistic. A blend of Cyanex272 and TOPO was found to be the most successful in separating the two metals. The extraction % for both metals increased as the HCl concentration increased, however the dependency of separation factor on HCl concentration was the reverse in both extracatant systems. The mixes resulted in a Zr and Hf extraction that was synergistic. A blend of Cyanex272 and TOPO was found to be the most successful in separating the two metals.

D2EHPA-uranium TOPO's (VI) extraction technique from a wet process phosphoric acid was carried out by Girgin*et al.*[38]. D2EHPA and TOPO diluted in technical grade kerosene were used to extract uranium from technical grade phosphoric acid. The effects of various parameters on uranium recovery, such as uranium oxidation stage, temperature, and the molar ratio of D2EHPA/TOPO, were shown to be in good agreement with prior studies. However, a thorough examination of the impacts of phosphoric acid concentration, organic concentration, and acid/organic phase ratios indicated that the mechanism of D2EHPA/TOPO synergism was fairly complex, and that it changed depending on the acid concentration.

Zinc extraction from ethylene glycol chloride solution using trioctylphosphine oxide (non-aqueous liquid-liquid extraction) (TOPO)was carried out by Matsui *et al.*[39]. Using a compound called zinc-65, researchers looked at how much zinc is divided between the toluene phase containing TOPO and the ethylene glycol non-aqueous phase containing either hydrogen or lithium chloride. In zinc-hydrogen or lithium-chloride-TOPO systems, ZnCl2-

2TOPO complexes may predominate, and only mononuclear zinc complexes appear to exist in the two phases of the two systems.

Picric acid is extracted from acid aqueous solutions using cyclohexane, trioctylphosphine oxide, and trioctyl amine as solventswas carried out by Serine *et al.*[40]. Picric acid (Hpic) was extracted from acid chloride solutions into cyclohexane using trioctylphosphine oxide (TOPO) and trioctylamine (TOA), and the UV-visible spectra of the organic phase was investigated. In the natural phase, however, the acid can only bond to one TOA molecule. The 1:1 association with TOPO only shows an absorption peak in the UV range, thus it's thought to be a molecular adduct with a hydrogen bond. While TOPO and its 1:2 d 1:1 association with TOA exhibit a visible absorption peak that is very similar to picrate ions, the extracts are thought to be ion pairs in which an electron moves from the hydrogen to the oxygen atom in the visible range.

Mohanty et al. [41] were the ones who carried it out. At low pH levels, researchers discovered that extracting blue peroxychromic acid from dilute HCl, H_2SO_4, and H_2O_4 media with 0.013M TOPO in benzene was measurable (0.02N). The effects of diluents on extraction as well as divergent ion effects have been studied. The extracted species was discovered to be $CrO(O_2)_2$.TOPO. This technique was used to determine Cr (VI) in mine water and tannery effluents.

Yamada et al.[42] successfully separated Cr(III) and Cr(VI) using Tri-n-octylphosphine oxide. In hexane, chromium aqueous solvent extraction was investigated using the solvent extractant TOPO. The kinetically inert Cr3+ is removed from a 1 mole perchlorate solution very fast and quantitatively as Cr $(H_2O.TOPO)_{63}+(ClO_4-)_3$. Chromium (VI) is extracted as H_2CrO_4 (HCl)n by hydrochloric acid. These findings led to the development of an extraction process for chromium in aqueous solution utilising 0.01 moles of TOPO in Hexane.

Extraction of Chromium was carried out by Rajiv Ranjan Srivastava *et al*.[43] by using TBP. The results of the experiments showed that increase in the extractant conc. improved the extraction % of Cr^{6+}. Analyses of the organic phase using thermodynamics and FTIR analysis revealed that exothermic extraction was also carried out. Ascorbic acid was used to reductively strip the loaded organic containing 5.0 g/L Cr_6+. Using a 1.5 M $C_6H_8O_6$ solution for 30 minutes, more than 99 percent of the metal was removed. With ammonia precipitation, the metal's less toxic form (Cr_3+ in stripped solution) was finally recovered at pH 9.0.

CHAPTER-4

EXTRACTION OF Cr(VI) USING TOPO AND CYANEX 272

EXTRACTION OF Cr(VI) USING TOPO AND CYANEX 272

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

4.1.1 SOLUTIONS AND REAGENTS

SYSTEM 1:

Choudhury P [44] extracted Cr(VI) from cyclohexane using the extractant TOPO(tri-n-octylphosphine-oxide). The required amount of Cr(VI) (4000ppm) was prepared. This TOPO was obtained from the company Heavy Metals, Talcher without further purification. As a diluent, cyclohexane was employed. Weighing the desired amount of extractant and diluting it in cyclohexane yielded the stock solution of TOPO (0.1M). Workable solutions were prepared by diluting both aqueous (100PPM) and organic (0.02M) stocks according to the requirements. Everything else that was used was of a high analytical grade.

SYSTEM 2:

Using the extractant Cyanex 272, Das S[45] extracted Cr(VI). $K_2Cr_2O_7$ in distilled water was used to dissolve the required amount of Potassium dichromate. Sigma-Aldrich provided a Cyanex272 sample that was used without further purification. As a diluent, cyclohexane was employed. It was prepared by weighing the desired amount of extractant and diluting it in Cyanex272 to make a stock solution of 0.1M. Aqueous (100ppm) and organic (0.02M) working solutions were prepared by diluting the aqueous and organic stocks according to the requirements. Everything else that was used was of a high analytical grade.

SYSTEM 3:

A mixture of TOPO and Cyanex 272 has been used by Kar A[46] to extract Cr(VI). Using Potassium Dichromate ($K_2Cr_2O_7$), the required amount of Cr (VI) (4000 ppm) was dissolved in double-distilled water. Topo and Cyanex 272 from Heavy Metals, Talcher and Cytec Inc. As a diluent, cyclohexane was employed. To prepare the stock solutions of TOPO (0.1M) and Cyanex 272 (0.1M), the extractants were weighed and then diluted in cyclohexane. We prepared aqueous (100ppm) and organic mixture solution (0.05 M TOPO + 0.05 M Cyanex 272) working solutions by diluting both the aqueous and organic stocks to the required concentration. 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, with no time variation. Using a UV-visible spectrophotometer and colour developing reagents (10 mL KSCN, 2mL N/2 HCl, 25 mL acetone) at 585 nm, the metal concentration was determined in the aqueous phase using UV Spectrophotometer (SYSTRONICS 105). It was possible to calculate how much metal ion was in the organic phase using distribution law equation. We carried out all of our research in a temperature-controlled environment.

4.2. RESULTS AND DISCUSSIONS

SYSTEM 1:

By Choudhury P[1] using the extractant TOPO.

Effect of equilibration time:

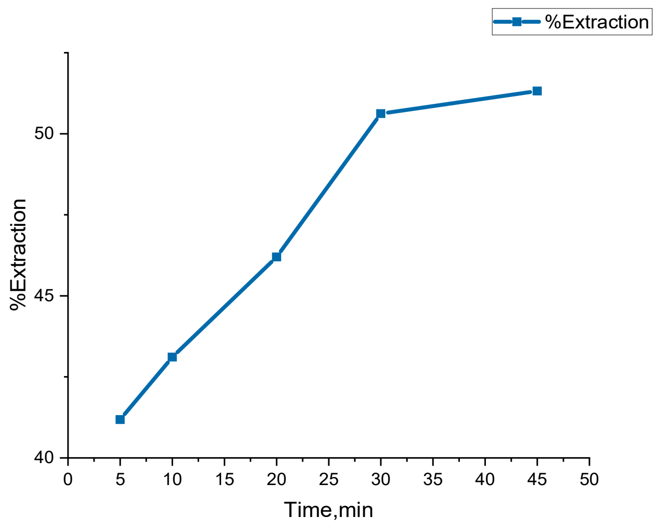


Figure 1

Effect of Aqueous phase pH :

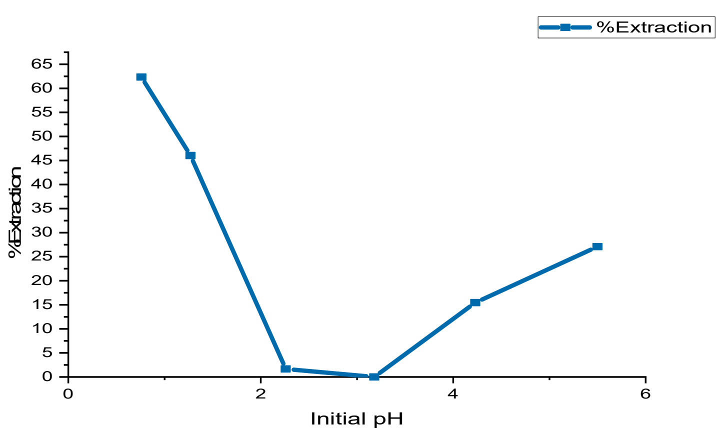


Figure 2

Effect of concentration of organic phase:

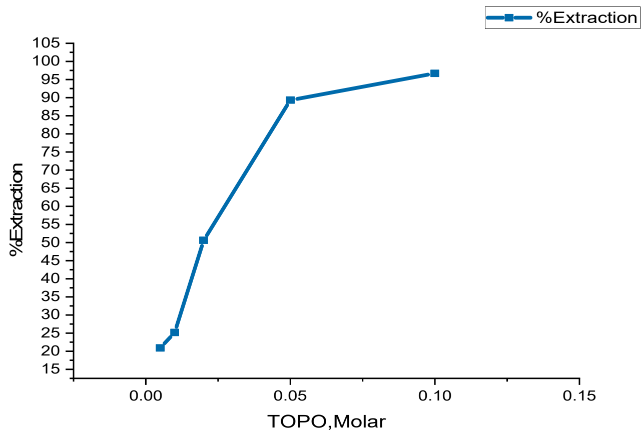


Figure 3

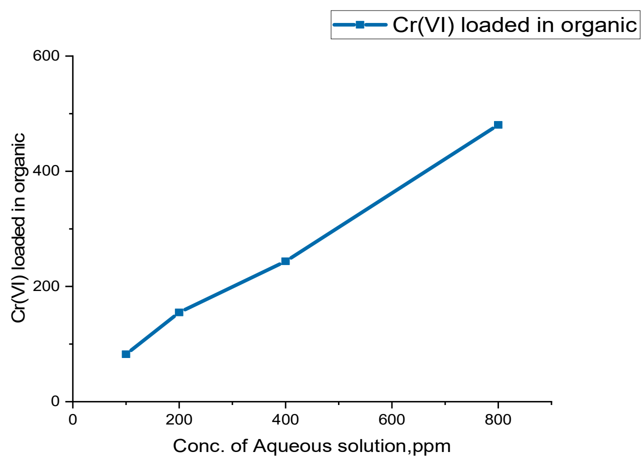


Figure 4

4.2.1 RESULTS:

•Equilibration time was reached at 30 minutes.

•The pH was maintained 1.27 throughout the experiment.

• Extraction % varied from 20.9% to 96.70% with increase in concentration of organic phase from 0.0025M to 0.1M.

•Extraction % decreased from 89.32% to 64.12% with increase in concentration of aqueous phase from 100ppm to 800ppm.

SYSTEM 2:

Extraction of Cr(VI) has been carried out by Das S[2] using the extractant Cyanex 272.

Effect of Equlibration time :

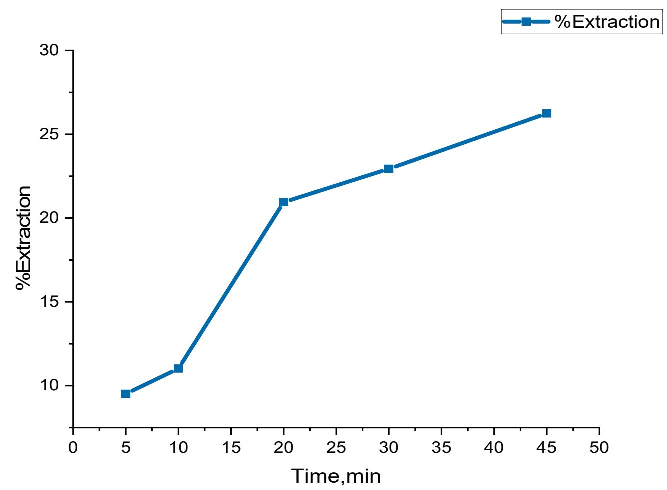


Figure 5

Effect of Aqueous phase pH:

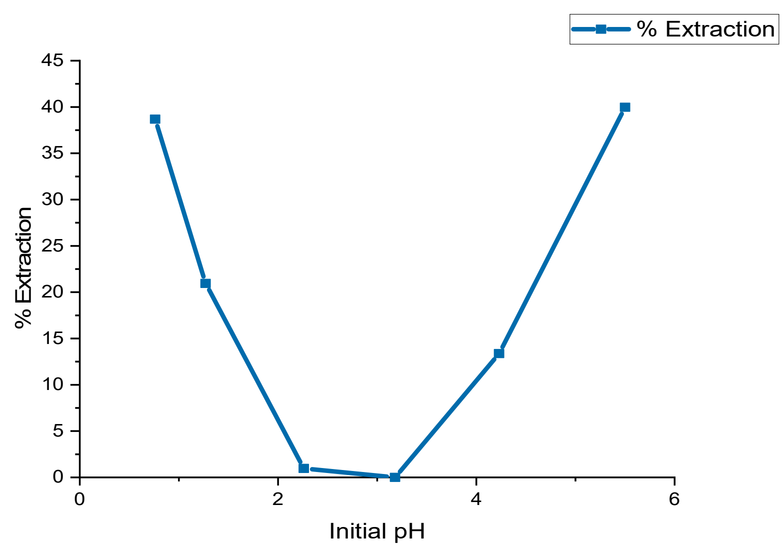


Figure. 6

Effect of concentration Organic Phase:

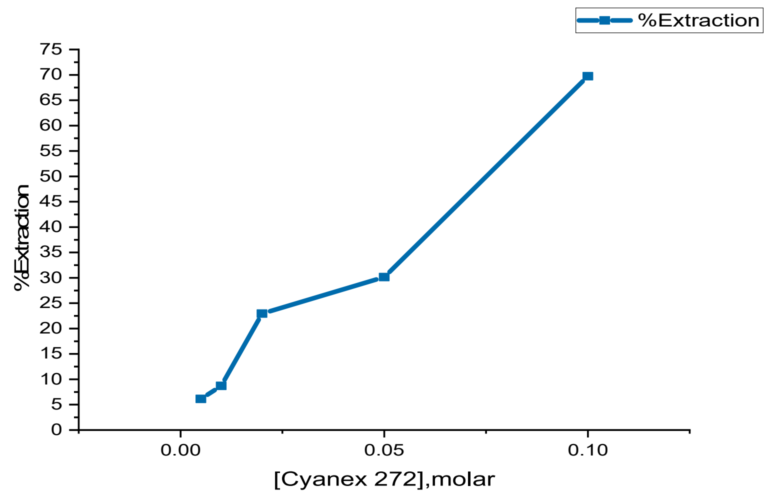


Figure.7

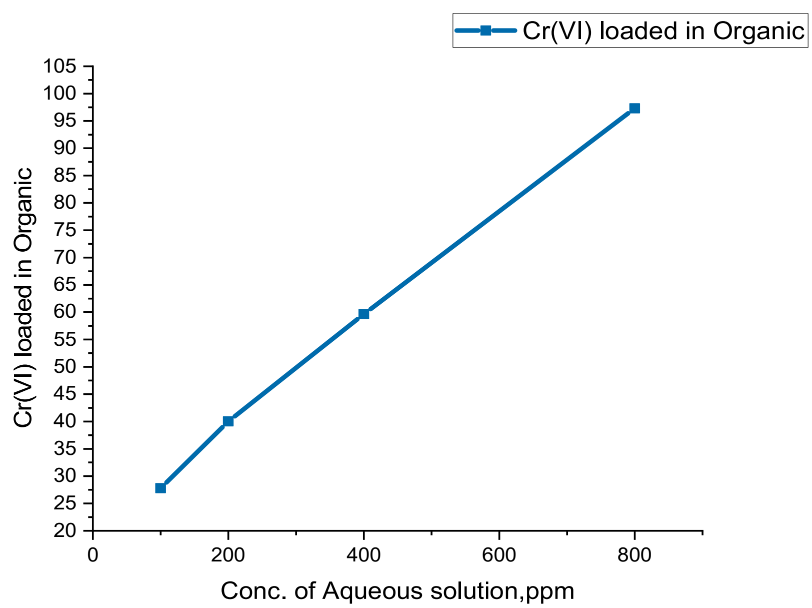


Figure.8

4.2.2 RESULTS:

- Equilibration time was reached at 30 minutes.
- Extraction% was 38.68% to 13.37% in the pH range 0.76 to 5.5. The pH was maintained 1.27 throughout the experiment.
- Percentage of extraction of Cr(VI) increased from 6.13% to 69.74% with increase in concentration of Cyanex272 from 0.005M to 0.1M.
- Extraction % decreased from 30.15% to 12.99% with increase in concentration of aqueous phase from 100ppm to 800ppm.

SYSTEM 3:

Extraction of Cr(VI) has been carried out by Kar A[3] using the mixture of TOPO and Cyanex 272.

Effect of equilibration time:

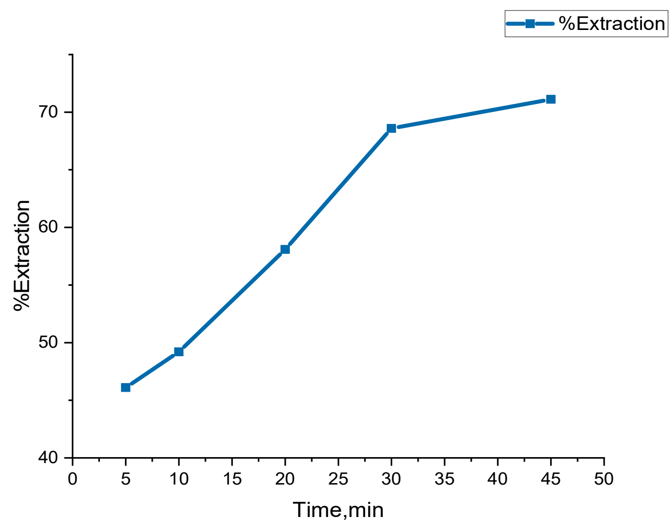


Figure.9

Effect of Aqueous phase pH:

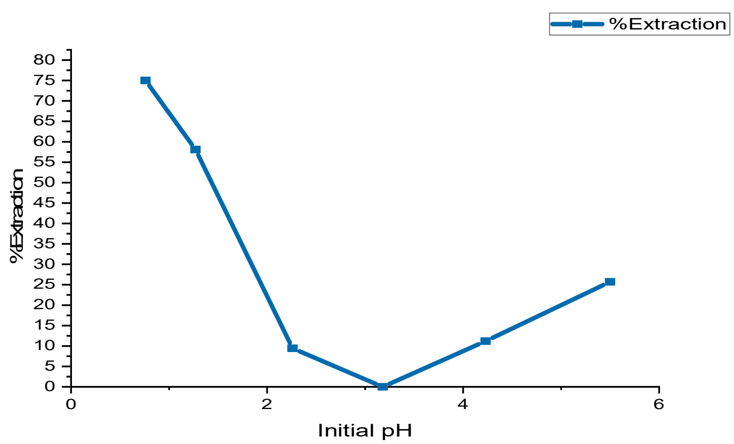


Figure.10

Effect of concentration of organic phase:

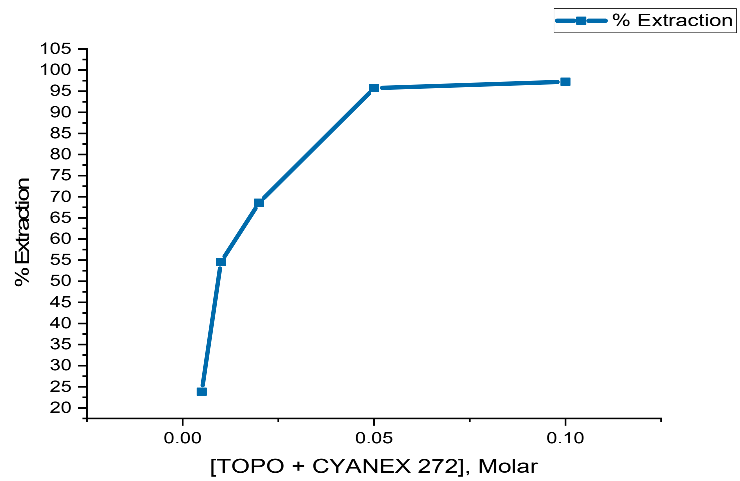


Figure.11. Effect of Different organic phase concentrations on chromium extraction at pH=1.27.

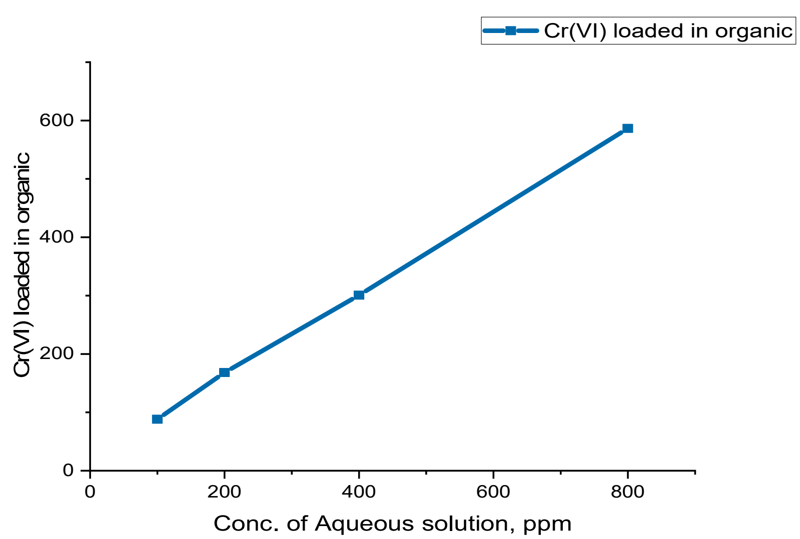


Figure.12. Effect of concentration of aqueous phase. Aq: 20 mL of Cr(VI) solution and Org: 20ml mixture of TOPO(0.05M) and Cyanex 272(0.05M) in cyclohexane at pH 1.27.

4.2.3 RESULTS :

- Equilibration time was reached at 30minutes.
- The highest percentage extraction of Cr(VI) is 62.35% using 0.02 M TOPO, 39.97% using 0.02 M Cyanex 272 and 75% using mixture of 0.02M TOPO & 0.02 M Cyanex272 was obtained at pH 0.76, 5.5 and 0.76 respectively.
- Percentage extraction of Cr(VI) increased from 23.84% to 97.24% in which organic solvent varied from 0.005 M to 0.1M.
- Percentage extraction of Cr(VI) changed from 95.72% to 78.28% in which aqueous phase varied from 100ppm to 800ppm.

CHAPTER-5

CONCLUSION

CONCLUSION

Literature has been surveyed from which it is observed that chromium has been effectively extracted using various extractants namely TOPO, TOA, Cyanex 272, tri-capryl amine Oxide, tri-butyl phosphate, tri-alkyl amine/kerosene etc, by the method of liquid-liquid extraction in the last decade. Effect of equilibration time, aqueous phase pH, 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:-

- By Li et al., the percentage extraction of chromium is 99.99% using trialkylamine.
- By Hariharan et al.,the Percentage extraction of chromium is 95% using Tricaprylamine Oxide.
- Cyanex 923 mixed with kerosene is used to remove chromium (VI) from industrial waste solution. was studied by Agrawal et al. in which extraction percentage of chromium is 98.6-99.9%.
- Hexavalent chromium recovery from acidic chloride media using liquid-liquid extraction with tributylphosphatewas studied by Ouejhani et al. in which extraction percentage of chromium is 90%.
- By Choudhury P et al., the percentage extraction of chromium is 96.70% using TOPO.
- Cr(VI) is extracted using Cyanex 272 in a liquid-liquid extraction method, was studied by Das S et al. in which extraction percentage of chromium is 69.74%.
- By Kar A et al., the percentage extraction of chromium is 97.24 using TOPO and Cyanex 272.

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