“STUDY OF RECOVERY OF PHOSPHORIC ACID FROM INDUSTRIAL WASTE WATER”

A

Minor Research Project

Submitted

To

UGC(WRO),Ganeshkhind,

Pune

UNDER THE DEPARTMENT OF CHEMICAL ENGINEERING

BY

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YEAR: 2013-2015

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MINOR RESEARCH PROJECT

The minor project work entitled **"Study of Recovery of Phosphoric Acid from Industrial Waste Water"** contains four Chapters (1) Introduction (2) Review of literature (3) Materials and methods and (4) Result and discussion followed by list of references cited throughout the project work.

Chapter1. Introduction

Acids : Acids are of two types

1. Organic Acid and 2. Inorganic Acid

An organic acid is an organic compound with acidic properties.

An inorganic acid is an acid derived from one or more inorganic compounds. All mineral acids form hydrogen ions and the conjugate base ions when dissolved in water. Examples of inorganic acids are Hydrochloric acid HCl, Nitric acid HNO_3, Phosphoric acid H_3PO_4, Sulfuric acid H_2SO_4, Boric acid H_3BO_3, Hydrofluoric acid HF, Hydrobromic acid HBr, Perchloric acid $HClO_4$.

Generally, industrial wastewater can be divided into two types: inorganic industrial wastewater and organic industrial wastewater [1].

Metal finishing operations are carried out by most of the industries engaged in forming and finishing metal products. The wastes from metal finishing industries include cleaning acids, sludge containing toxic heavy metals, solvents and oils, and spent chromate and cyanide

solutions, which are classified as hazardous substances [2].Inorganic acids are used in various processes. Nitric acid is used in Printed Circuit Board (PCB) manufacture[3].Nitrations of aromatic compounds have been carried out with the use of a mixture of nitric acid and sulfuric acid for manufacturing of various nitro products[4].

Various industries produce different compositions of different spent inorganic acids. But huge quantity of SPL is generated every year e.g. 3,00,000 m^3 /year [5] .In this report research was concentrated on recovery of inorganic acids such as hydrochloric acid, sulfuric acid and phosphoric acid from spent pickle liquor of electroplating and steel industry.

Pickling is the process of removal of oxide layer and rust formed on metal surface. It also removes sand and corrosion products from the surface of metal. Acids such as sulfuric acid, hydrochloric acid are used for pickling. Hydrofluoric acid-Nitric acid mixture is used for stainless steel pickling. Phosphoric acid is used for pickling of automobile components parts. Pickling solutions are spent when acid concentration in them decreases by 75-85%, which also has metal content up to 150-250 g/dm^3.The acid after pickling is termed as spent pickle liquor (SPL).

SPL should be dumped because the efficiency of pickling decreases with increasing content of dissolved metal in the bath. The SPL content depends on the plant of origin and the pickling method applied there. In USA 1400 million gallons of spent pickle liquor is produced annually while in European Union generation rate of spent pickle liquor is 3 lakh m^3/year .In India spent pickle liquor generation rate is 240 m^3 /year[1].

SPL from steel pickling in hot-dip galvanizing plants contain zinc (II), iron, traces of lead, chromium and other heavy metals (max. 500mg/dm^3) and hydrochloric acid. Zinc (II) passes to the spent solution after dissolution of this metal from zinc (II)-covered racks, chains and baskets used for transportation of galvanized elements.

Highly acidic untreated spent pickle liquor cannot be directly discharged to receiving surface water. If discharged to surface water ferrous salts in the wastewater are oxidized at the expense of the dissolved oxygen in the receiving water to ferric compounds, which are deposited in the water bodies as reddish brown sediment.

Spent pickle liquor if allowed to percolate into ground contaminates the subsoil water with dissolved iron and salts. Iron, even in very small quantities is undesirable in water for domestic supply as it may give rise to growths of "iron bacteria" which forms a gelatinous mass containing the iron oxide which is an end product of their metabolic processes and also render the water unaesthetic. Inhalation of acid fumes creates health problems for workers. Such wastes therefore warrant adequate treatment before discharge in receiving water bodies [6].

Recovery and regeneration of acid from pickling step is recommended to limit the use of chemicals and discharge of harmful emissions to water bodies and the air.

In this project work attempt has been made to study the recovery of inorganic acid such as phosphoric acid from spent pickle liquor of steel and electroplating industry by evaporation method.

Chapter2. Review of Literature

Extensive review of literature was carried out for the study of recovery of inorganic acids such as hydrochloric acid, sulfuric acid and phosphoric acid from spent pickle liquor of steel and electroplating industry.

Horwitz et al. developed phosphoric acid [7] purification by the adsorption of the acid on ion exchange resins. Acids such as phosphoric acid contaminated with multivalent metal salts are purified by a process which involves treatment in an acid sorption unit (ASU) and a nanofiltration unit (NFU) in the process patented by Craig J. Brown 1996 [8].Maranon et al 2000 studied the two types of anionic ion exchange resins, Lewatit MP-500 and Lewatit M-504 to remove iron and zinc from acid pickling bath to maintain the concentration of both metals within level to improve the life of bath [9].

A new process for separation of strong acids from metal salts was introduced by Hatch et al 1963 called 'acid retardation', the process was used for purification of waste acids generated in pickling metals and leaching ores [10]. Research was carried out by H. Tan 1996[11] for separation of acid salt separation by ion exchange resins. Using different anion exchangers, it was possible to remove Zn(II) and Fe effectively from spent hydrochloric acid from steel pickling as per the study performed by Ireneusz Miesiac et al 2010[12]. Adsorption of iron for recovery of phosphoric acid etc. was studied by A. Ortiz. et al [13]. P. Kittissupakora et al 2005 studied modeling for HCl recovery from SPL [14].

Dr. Stefan Neumann 2012 has discussed the ion exchange resins in electroplating industry for recovery of acids from wastewater [15].Recovery and recycle of spent pickling acids was studied

by G. Thornburg [16]. The methodology used in research was by conducting experiment of regeneration of Hydrochloric acid using Kleingarn acid management system by N. Muthuet al 2013, collecting experiment data and calculating the short and long term cost reduction that can be achieved [17]. Membrane distillation was carried out by Inga B. Elkina et al 2013 for the regeneration of volatile inorganic acids (Hydrochloric and Nitric acids)[18]from the metal pickling solutions using special membranes. C.J. Jewel et al 1986 developed process to recover Hydrochloric acid using Fluidized Bed Reactor[19].

Cattrall andWest1966 [20]extracted sulfuric acid by alcohols. Petkovic et al[21]studied the extraction of mineral acids such as hydrochloric acid, nitric acid and sulfuric acid using tri-n-octylphosphine oxide with carbon tetrachloride as the diluents. Agrawal et al[22] studied the solvent extraction of concentrated sulfuric acid from sulfate waste pickle liquors using Cyanex 923(trialkylphosphine oxide (TRPO)).The solvent extraction of sulfuric acid from sulfate waste pickle liquor of iron and steel tubes using Alamine 336 has been studied in detail by Agrawal et al [23].

Sarangi et al [24] carried out the study for removal/recovery of hydrochloric acid from a waste pickle liquor of a secondary waste, using extractants such as TBP, Cyanex 923,Alamine 336 and Aliquat 336.A review on spent pickling liquor was studied by A. Devi et al [25].

A phosphoric acid reclamation process in combination with an Al pickling process having a pickling bath has been developed by Hjersted, N B which includes evaporation and crystallization [26].

Chapter3.Materials and Methods

Materials: Spent pickle liquor (SPL) containing Phosphoric acid was collected from a local automobile industry. The chemicals used for analysis of SPL containing Phosphoric acid were of S D Fine Chemicals Ltd., Mumbai and Qualigens Chemicals, Mumbai.

Physicochemical characteristics of SPL

A. Analysis of SPL

Analysis of SPL was carried out by APHA method as well as by standard methods adopted in industry. This included free acid determination of H_3PO_4,determination of heavy metals like Fe, Zn, Pb, Cd,Ni and Cu, pH of the , Total dissolved solids(TDS), Total suspended solids(TSS), Specific gravity, Chlorides and Boiling point.

i) Determination of free acid in spent pickle liquor

Phosphoric acid content in spent pickle liquor and in recovered phosphoric acid was determined by the method given by M. Lynch [28].

ii) Determination of heavy metals

The concentration of heavy metals like Fe, Zn, Pb, Cd, Ni and Cu present in spent pickle liquors were determined by the standard methods given in APHA (American Public Health Association) [27].

iii) Determination of pH:

pH of the spent pickle liquor was determined by usual standard methods.

HPLC Younglin Model Acme 9000 was used for analysis of recovered Phosphoric acid. All reagents used were of HPLC grade.

Recovery of Phosphoric acid from Spent Pickle Liquor by evaporation method:

Evaporation process was carried out using evaporation apparatus which included 5 litre round bottom flask with heating mantle, a condenser & receiver. A known volume of SPL sample was taken in the round bottom flask, and the flask was heated till it was boiled and formed vapours of acid. The vapours of acid formed were condensed and collected in a condensate receiver. The % free acid in condensate was estimated with time till constant reading was obtained.

Chapter4. Result and Discussions

A. Analysis of SPL and Composition of SPL

The analysis of SPL containing Phosphoric acid is reported in Table.1. It was found that the SPL contains Fe in large quantity followed by Zn and Cu. The other metals include Pb, Cd, and Ni in SPL. pH was 3 , 0.51% free acid for SPL containing Phosphoric acid [Table 1].

I. Recovery of acids:

Acid recovery by evaporation:

The recovered acid by evaporation method was analyzed and with the above results as shown in Tables 2. From the confirmatory tests it was found that the recovered acid was Phosphoric acid. From the parameters such as pH, boiling point and specific gravity it has been confirmed that the acid present in sample (SPL) was dilute and its quantity in sample was near 0.5 to 5 % for phosphoric acid.

Salient findings

- Analysis of SPL revealed that the values obtained for different parameters are in the range available in the literature
- SPL contains Free acid, Iron, Zinc, Chromium, Lead etc.
- The % iron content in the effluent samples was found to vary from 0.040 to 0.044 (w/v)
- The acid recovery was 30-40%

Conclusion

Evaporation Method:

The spent pickle liquor i.e. sample was analyzed and result was drawn and it stated that phosphoric acid was present in the sample. Also, the acid was recovered and analysis was done and result was given which has stated that the percentage of acid in SPL was 0.5 to 5 %. Advantage is that the acid which was recovered can be further used in pickling processes. However,the evaporation process is energy intensive and costly.

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Table 1:Analysis of SPL(Phosphoric acid) from local automobile industry

Component	Zn (mg/l)	Pb (mg/l)	Cd (mg/l)	Ni (mg/l)	pH	Fe(mg/l)	Cu (mg/l)	Phosphoric acid (g/l)
Concentration	21.25	11.19	0.73	9.48	3.00	39.69	8.28	5.10

Table 2: Analysis of Recovered Phosphoric Acid

Sr. No.	Parameter	Values
1	pH	4.8
2	Density	1.0052 kg/m^3
3	Specific Gravity	0.9665
4	Total Dissolved Solid	26.82gm/l
5	Acid Determination	5.2 w/v%
6	Iron Determination	6.081 w/v% Fe

Bio-Data

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Academic Record

Degree	University	Year	Subject	Marks	Division
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M. E. Dissertation:"Treatment of spent pickle liquor of steel industry with recourse to recovery of hydrochloric acid"

Teaching Experience: Undergraduate: 11 Years and Postgraduate: 00 Years

Name of College	**Designation**	**Duration**	**Subjects taught**
ShriDattaMeghe Polytechnic,Nagpur	Lecturer	December1998 to April 2000 July2007 to May 2008	Plant Engineering,PlantUtilities,Chemical Technology-I, Chemical Reaction Engineering
Nagpur Polytechnic, Nagpur	Lecturer	July 2005 to May 2007	Plant Engineering, Plant Utilities, Chemical Technology-I, Chemical Reaction Engineering, Industrial Pollution & Control
SSBT's, College of Engineering and Technology, Bambhori, Jalgaon.	Assistant Professor	July 2008 till date	Process Dynamics & Control, Chemical Processes-I, Fluid Flow & Solids Handling, Chemical Engineering Thermodynamics, Mass Transfer-II, Process Calculations ,Transport Phenomena

List of papers published in journals:

1. Nikhil Ghare,VijayKulkarni,PurushottamKhanna "Source reduction and cleaner technologies for select industries", Chemical Industry Digest,August 1995, 93-102.

2. V. Kulkarni,NikhilGhare,P.Khanna **"**Cleaner technologies for select industries" Productivity,April- June 1994,pp. 74-81.

3. Nikhil Y. Ghare, M.Sureshkumar,A.S. Vaidya&A.N.Bal "Recovery of acid from pickling liquors" Environmental Engineering Science,Volume 15, No. 4,1998,pp. 259-263.

4. N.Y.Ghare,A. Bakore,V.Kulkarni&P.Khanna "Cleaner technologies of Industrial Production-Indian Scenario"Tech Monitor,March- April 1994, pp.54-61.

5. N. Y. Ghare , K. S. Wani and V. S. Patil"Recovery of acids from spent pickle liquor of a steel industry by ion-exchange route" International Journal of Emerging Trends in Engineering and Development Issue 4, Vol.1 (January 2014)pp. 318-326.

List of papers published in national and international conferences:

1. AtulkumarBakore,VijayKulkarni,**Nikhil Ghare**&PurushottamKhanna,"CleanerTechnologies Case Study Data Base at NEERI,India" ENTRÉE'94,Nov.16-19,1994,Finland.

2. **N.Y.Ghare**, K.S.Waniand V.S.Patil, "Recovery of Hydrochloric Acid from Spent Pickle Liquor of Steel Industry", Published in National Conference on "Emerging Trends in Engineering, Technology and Management", held on 29th March 2010, organized by SSBT's C.O.E.T.,Bambhori, Jalgaon.

3. **N.Y.Ghare**,Dr.K.S.Wani& Dr. V.S.Patil "Analysis and recovery of Sulfuric acid from Spent Liquor of Electroplating Industry" in National Conference on Environmental Innovations for Resource Sustainability,atNMU,Jalgaon,on 21-22 January 2011.

4. N.M. Limaye, **Nikhil Ghare**, " Cost effective method of recovery of Zn^{2+} ions from binary mixtures with Na^{+},Mn^{2+}, Mg^{2+},$Ca^{2+,}$ Ba^{2+} &Sr^{2+} using an ion exchanger loaded with chelating molecules of 8-hydroxyquinoline-5 sulphonic acid "in International Conference onAdvances in Energy Technology",atSSBT's C.O.E.T.Bambhori, Jalgaon.,on29th March 2013.

Research funding granted:

1. Rs. 30,000/- was sanctioned by Institution of Engineers (India) , Kolkata for student project titled **"Recovery of Acids (Sulfuric/Nitric Acid) from Industrial wastewater"**in year 2009-2010 under guidance of Shri N. Y. Ghare. The project was completed.

2. Rs. 1,17,000/- is sanctioned for Minor Research Project by University Grants Commission ,Western Regional Office, Pune , for project titled **" Study of Recovery of Phosphoric Acid from Industrial wastewater"** in year 2012-2013. Principle Investigator of project is Shri N. Y. Ghare. The project is completed.

Work involvement at institute and departmental level:

1.Member, Antiragging committee of institute

2. Had worked as Member, Admission committee of institute

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Workshop/STTP attended:

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2. Attended three days National Level Workshop on "Research Methodology" organized by Department of Mechanical Engineering & Department of Business Administration, at SSBT's C.O.E.T.,Bambhori, Jalgaon during October 17-19, 2011.

3. Attended three days Teachers Training Workshop on "ShramSadhana" organized by SSBT's C.O.E.T.,Bambhori, Jalgaon and Deeepstambh Foundation, Jalgaon during July 9-11, 2009.

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