

Treatment of Spent Pickling Liquor and Applications of Pickling Sludge

THESIS

Submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

ANURADHA DEVI
ID No. 2012PHXF0006P

Under the Supervision of

Dr. Anupam Singhal,

Prof. Rajiv Gupta

&

Prof. S. K. Verma



BITS Pilani
Pilani | Dubai | Goa | Hyderabad

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE, PILANI

2017



**BIRLA INSTITUTE OF TECHNOLOGY & SCIENCE
PILANI – 333 031 (RAJASTHAN) INDIA**

CERTIFICATE

This is to certify that the thesis entitled **“Treatment of Spent Pickling Liquor and Applications of Pickling Sludge”** submitted by **Anuradha Devi**, ID No. **2012PHXF0006P** for the award of Ph.D. of the Institute embodies original work done by her under our supervision.

Signature of the Supervisor

Name: ANUPAM SINGHAL

Designation: Associate Professor

Date: / / 2018.

Signature of the Co-Supervisor

Name: RAJIV GUPTA

Designation: Senior Professor

Date: / / 2018.

Signature of the Co-Supervisor

Name: S. K. VERMA

Designation: Professor

Date: / / 2018.

Acknowledgment

I would like to take this opportunity to convey my heartfelt gratitude and indebtedness to my Gurus for all their support, guidance and supervision during my research tenure. At the outset, I wish to express the deep sense of gratitude and sincere thanks to my Guru Dr. Anupam Singhal (Associate Professor), Prof. Rajiv Gupta (Senior Professor), Department of Civil Engineering and Prof. S K Verma (Professor), Department of Biological Science for their valuable guidance, encouragement, suggestions, and moral support throughout the period of this research work.

I would like to take this opportunity to express my gratefulness to Prof. Suresh Gupta and Prof Jitendra Panwar, who are the members of Doctoral Advisory Committee (DAC), for their kind suggestions, motivation and moral support throughout the program both technically and personally.

I express my deep sense of appreciation to BITS Pilani for providing all the necessary facilities and support to complete the research work. My special thanks to Prof. S. Bhattacharyya, Vice-Chancellor of the University, Prof. A. K. Sarkar, Director, BITS-Pilani, Pilani Campus for allowing me to pursue my research work successfully. I also express my gratitude to Prof. S.K. Verma, Dean, Academic Research and other faculty members of ARD for providing valuable support throughout the programme. I would like to thank Prof. R K Mittal, HoD, Civil Engineering for their motivation during difficult times.

I am also thankful to all my professors notably Prof. S. B. Singh, Dr. Manoj K., Dr. Kamalesh Kumar, Dr. D. Bhunia, Dr. S. N. Patel, Dr. Anshuman, Dr. G. Muthukumar, Dr. A. Goel, Dr. Bahurudeen for their support and motivation throughout my studies at BITS-Pilani, Pilani Campus. I am also thankful to all laboratory and secretarial staff for their timely support. I also thank all my friends, especially Arun Nihal Singh, Nikita, Priya, Amrita, Dilawar, Omkar, Kanika, Rajesh, Gaurav, Himanshu, Pankaj, Rahul, Jitendra, Satish, and all others whose name are not here and have helped me during my Ph.D. Thanks are also due to all faculty and staff members of BITS-Pilani, Pilani Campus for helping me out at various times.

Last but most importantly, I thank my parents and my sister for their care and affection shown towards me to undertake this journey. My thanks are also extended to the universe that has enlightened me with the gift to see the truth beyond the boundaries as a part of the cosmic play. May, I would cherish happy moments spent at BITS Pilani campus for the whole life.

Anuradha Devi

In steel industries, pickling process generates a considerable quantity of Spent Pickle Liquor (SPL) containing the dissolved metal salts of iron as well as residual free acid. The waste generated by metal pickling industries is identified as hazardous solid waste as per Indian Standards and United State Environmental Protection Agency (US EPA). The treatment methods of nitric acid and hydrofluoric acid mixture are better developed than of hydrochloric or sulfuric acid because of the great amount of spending pickling solution from stainless steel pickling. But spent pickling solution from mild steel pickling cannot be neglected as it is hazardous in nature and has a detrimental effect on the environment. Thus, in the present thesis emphasis are given to treatment methods of pickling liquor of mild steel pickling.

Various types of recovery and regeneration methods are used to recover and regenerate the acid and metals from the SPL. Nevertheless, these methods are sumptuous and not amenable for small-scale industries. In developing country like India, where lots of micro, small and medium scale industries exist, only precipitation is a pecuniary treatment method but it generates lots of sludge. There are severe problems in its disposal to lined sites (landfills). Thus, the study has been undertaken to minimize the generation of the pickling sludge by different neutralizing agents and their combination with economic valuation along with sludge characterization. The results show that the treatment of pickling effluent with lime is the economical solution but the quantity of sludge generation is on a higher side. However, we recommend 20% calcium hydroxide and 80% sodium hydroxide for the treatment; because sludge reduction is appreciable and lower sludge generation will result in lower cost of sludge handling.

Biosorption is an environmentally friendly method treatment of domestic and industrial effluent. The major advantages of biosorption over other treatment methods include low cost; high efficiency; minimization of chemicals; no additional nutrient requirement; regeneration of absorbent; the possibility of metal recovery & no sludge generation. Hence, an attempt has been made to treat SPL by biosorption method. In this study, *Scenedesmus* sp. was used as an inexpensive and efficient biosorbent for SPL that contains iron ions. The effect of various physicochemical factors on Fe (II) biosorption such as pH 1.0–7.0, initial metal concentration (0.0–500 mg/l) and contact time (0–180 min) were studied. In the light of experimental results obtained and their evaluation, microalgae could be considered a potential adsorbent for the removal of iron from aqueous solutions. FTIR analysis of the biosorbent, before and after iron sorption, revealed

that amine and hydroxyl groups could be involved in metal binding to the algal biomass. Experimental data can be described adequately by the pseudo-second-order kinetic confirming the chemisorption of iron on the algal surface. Continuous adsorption studies revealed that microalgae (*Scenedesmus* sp.) could be successfully used as biosorbent for treating effluents containing Fe (II).

The neutralization treatment method produces a large amount of sludge. Pickling sludge disposal is a huge problem as land disposal restrictions are becoming ever increasingly strict, driven by the technical, regulatory and political considerations. Hence, an attempt has been made to investigate the feasibility of utilizing the industrial waste as fertilizer for the ornamental plant. Pickling sludge and copper industry tailing waste were used as a fertilizer in oleander plantation. The height of plant results shows that the copper tailing and pickling sludge mixture generates promising results. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis was performed to study the effect of heavy metals in plants uptake. Barium (Ba) was present in the soil of study area and the plant uptake the Ba as a contaminant. It has been observed that Ba uptake by oleander plants was reduced by 90% may be due to the presence of calcium and silica in pickling sludge and copper tailing. The other heavy metals present in industrial wastes have any significant effect on plant uptake.

The pickling sludge contains heavy metals that may contaminate the groundwater by leaching during the rainy season. Consequently, an effort has been made to test the potential of utilizing Solidification/Stabilization (S/S) pickling sludge in pavement tiles as a partial replacement for cement. Pavement tiles prepared by a concrete mix of 1:2:4 (Cement: Sand: Stone grit) for the study. The Physical (Block Density, Absorption, Drying Shrinkage and Compressive strength) and Toxicity Characteristic Leaching Procedure (TCLP) test have been carried out. The outcomes indicated that the pickling sludge can be used in pavement tiles as a partial replacement of cement up to 10%. This will not only help in solving the disposal problem but also reduce the manufacturing cost of tiles.

Keywords: *Spent pickling liquor, Sludge minimization, Sludge utilization, Biosorption.*

List of Contents

Contents	Page
Candidate Declaration	<i>ii</i>
Acknowledgement	<i>iii</i>
Abstract	<i>iv</i>
List of content	<i>vi</i>
List of Figures	<i>xii</i>
List of Tables	<i>xiv</i>
Abbreviations	<i>xvi</i>
Chapter 1: Introduction	1-13
1.1 Background	2
1.2 Legislations	5
1.3 Formulation of Problem	7
1.4 Scope and Objectives	10
<i>References</i>	11
Chapter 2: Literature Review	14-51
2.1 Introduction	15
2.2 Established Method: Neutralization/ Precipitation	15
2.2.1 Solidification/Stabilization	16
2.3 Recovery of Metals and Acid	23
2.3.1 Evaporation and crystallization	23
2.3.2 Pyrohydrolysis	24
2.3.3 Solvent extraction (SX)	26
2.3.4 Low temperature crystallization	29
2.3.5 Membrane separation	30
2.3.5.1 Reverse osmosis and nano-filtration	31
2.3.5.2 Diffusion dialysis	31

	Contents	Page
	2.3.5.3 <i>Membrane distillation</i>	32
	2.3.5.4 <i>Other options</i>	32
2.4	Biosorption	34
2.5	Research Gaps	35
	<i>References</i>	37
Chapter 3:	Treatment of SPL	52-101
3.1	Introduction	53
3.2	Sample Collection and Preservation	53
3.3	Minimization of Sludge Generation	54
	3.3.1 Material and procedure	55
	3.3.2 Characterization of spent liquor and treated liquor	56
	3.3.2.1 <i>XRF study</i>	59
	3.3.2.2 <i>XRD analysis</i>	59
	3.3.2.3 <i>Particle size analysis</i>	60
	3.3.2.4 <i>pH Value</i>	60
	3.3.2.5 <i>Bulk density</i>	60
	3.3.2.6 <i>Moisture content of the sludge</i>	61
	3.3.2.7 <i>Loss on ignition</i>	61
3.4	Results and Discussions	61
	3.4.1 Characteristics of spent pickling liquor sample	61
	3.4.2 Result of treated SPL	62
	3.4.3 Sludge generation	65
	3.4.4 Economics analysis	66
	3.4.5 Characterization of treated sludge	67
3.5.	Discussions	71
3.6	Biosorption of Spent Pickling Liquor	72

	Contents	Page
3.6.1	Microalgae cultivation	72
3.6.2	Batch study	74
	3.6.2.1 <i>Effect of adsorbent concentration</i>	74
	3.6.2.2 <i>Effect of contact time</i>	74
	3.6.2.3 <i>Effect of initial concentration</i>	75
	3.6.2.4 <i>Infrared analysis</i>	75
	3.6.2.5 <i>Isotherms</i>	75
	3.6.2.6 <i>Kinetics</i>	77
	3.6.2.7 <i>Continuous study</i>	78
3.6.3	Thomas model	80
3.6.4	Yoon–Nelson model	81
3.7	Results and Discussions	82
3.7.1	Batch biosorption experiments	82
	3.7.1.1 <i>Effect of pH</i>	82
	3.7.1.2 <i>Effect of adsorbent dose</i>	84
	3.7.1.3 <i>Effect of contact time and initial metal ion concentration</i>	85
	3.7.1.4 <i>Biosorption kinetics</i>	87
	3.7.1.5 <i>Biosorption isotherms</i>	88
3.7.2	Continuous biosorption experiments	91
3.7.3	FTIR Analysis	95
3.8	Discussion	97
	<i>References</i>	98
	Chapter 4 Application of pickling sludge	102-149
4.1	Introduction	103
4.2	Investigations on the Feasibility of Utilizing Sludge as Fertilizer	103
	4.2.1 Material and procedure	103

	Contents	Page
	4.2.1.1 <i>Principle of ICP-AES</i>	104
4.2.2	Results and Discussions	105
	4.2.2.1 <i>Characterization of copper tailings and pickling sludge</i>	105
	4.2.2.2 <i>Influence of copper tailings</i>	110
	4.2.2.3 <i>Influence of sludge produced from spent pickling liquor</i>	110
	4.2.2.4 <i>Influence of combination of both copper tailing and sludge</i>	111
	4.2.2.5 <i>Heavy Metals: Barium, Silica and Arsenic</i>	111
	4.2.2.6 <i>Macronutrients: Sulfur, Phosphorous, Magnesium, Sodium and Calcium</i>	112
	4.2.2.7 <i>Micronutrients: Boron, Chlorine, Copper, Manganese, Iron, Molybdenum, and Zinc</i>	112
4.2.3	Discussions	113
4.3	Investigations on the Feasibility of Utilizing Sludge in Interlocking Tiles	114
4.3.1	Materials and Procedure	114
	4.3.1.1 <i>Preparation, casting and curing of specimens</i>	114
4.3.2	Cement	116
	4.3.2.1 <i>Chemical properties of cement</i>	116
	4.3.2.2 <i>Physical properties of the cement</i>	121
	4.3.2.3 <i>Fine aggregate (Sand)</i>	124
	4.3.2.4 <i>Coarse aggregate</i>	127
	4.3.2.5 <i>Casting of Tiles</i>	128
	4.3.2.6 <i>Physical and chemical properties of tiles</i>	131
	4.3.2.6.1 <i>Block Density</i>	131
	4.3.2.6.2 <i>Absorption</i>	131
	4.3.2.6.3 <i>Drying shrinkage</i>	131
	4.3.2.6.4 <i>TCLP test</i>	131
	4.3.2.7 <i>Compressive strength</i>	132

Contents	Page
4.3.3 Results and Discussions	133
4.3.3.1 <i>Characterization of the pickling sludge</i>	133
4.3.3.2 <i>Sieve analysis of sludge</i>	134
4.3.3.3 <i>Chemical Composition and Physical Properties of the Cement</i>	135
4.3.3.4 <i>Fine Aggregate (Sand) Analysis</i>	135
4.3.3.5 <i>Coarse Aggregate</i>	137
4.3.3.6 <i>TCLP test</i>	137
4.3.3.7 <i>Block Density</i>	138
4.3.3.8 <i>Absorption</i>	139
4.3.3.9 <i>Drying Shrinkage</i>	140
4.3.3.10 <i>Compressive strength</i>	141
4.3.4 Cost analysis	144
4.3.5 Discussions	145
<i>References</i>	146
Chapter 5: Conclusions and Future scope	150-153
5.1 Conclusion	151
5.2 Further scope of the work	154
Annexure	155-166
Annexure A: Status of hazardous waste generation in India	155
Annexure B: Specification of UV Spectrophotometer	157
Annexure C: Acid Soil Region (ASR) in India	158
Annexure D: Specification of FTIR	159
Annexure E: Specification of peristaltic pump	160
Annexure F: Time optimization for Fe (II) reduction with five biosorbents	161
Annexure G: Height of plant study on sludge as a fertilizer	163

Contents	Page
Annexure H: Particle size distribution graph of pickling sludge	164
Annexure I: Batch and continuous study	165
Annexure J: Culture of <i>Scenedesmus</i> sp .algae	166
Annexure K: Picture of instruments used during Thesis work	167
List of Publications	168
Brief biography of Candidate	170
Brief biography of Supervisor	171
Brief biography of Co-Supervisor	172
Brief biography of Co-Supervisor	173

List of Figures

Figure No.	Title	Page
1.1	Status of hazardous waste generation in India	3
1.2	Pickling waste generated in the steel streamline	3
1.3	The basic galvanizing process steps and likely emission points	8
2.1	Scheme of spray roasting process for SPL regeneration	25
2.2	Pickling hydrochloric acid regeneration layout	30
3.1	Sequence of steps involved in the treatment process	55
3.2	pH and TDS meter	57
3.3	DO meter	57
3.4	COD Digestor	57
3.5	Spectrophotometer DR2700	57
3.6	Evolution 201 UV-Visible Spectrophotometers	58
3.7	Rigaku Miniflex II, Benchtop X-ray Diffractometer	60
3.8	Colors of treated sludge	63
3.9	Graph showing the EC & TDS values of SPL treated samples	64
3.10	Percentage removal of total dissolved solids	64
3.11	% reduction in sludge generation vs cost of solution require for treatment of 200 ml sample	67
3.12	XRD spectrum of Sample N	68
3.13	XRD spectrum of Sample K	68
3.14	XRD spectrum of Sample LH	69
3.15	Flow diagram of continuous study for biosorption study	79
3.16	Effect of pH on Fe (II) uptake by microalgae	83
3.17	Effect of adsorbent dose on Fe (II) uptake by microalgae	84
3.18	Effect of contact time and initial Fe (II) ion concentration	86
3.19	Pseudo first-order plot for the biosorption of Fe (II) by microalgae	87
3.20	Pseudo Second-order plot for the biosorption of Fe (II) by microalgae	88

3.21	Langmuir Isotherm for biosorption of Fe (II) by microalgae	89
3.22	Freundlich Isotherm for biosorption of Fe (II) by microalgae	90
3.23	Breakthrough curve for biosorption of Fe (II) on microalgae in continuous study	92
3.24	Thomas model for biosorption of Fe (II) on microalgae in continuous study	93
3.25	FTIR spectrum of unused microalgae	96
3.26	FTIR spectrum of used microalgae	96
4.1	Basic components of ICP-AES	104
4.2	Sequence of dry sludge produced from wet sludge	114
4.3	Different shapes of tiles	115
4.4	Hand feed concrete mixer used in the study	128
4.5	Casting of tiles	129
4.6	Tiles used in the study	130
4.7	Orbital shaker for TCLP test	132
4.8	Compressive strength test of the tiles	133
4.9	XRD spectrum of B tile sample	142
4.10	XRD spectrum of D tile sample	143
4.11	XRD spectrum of F tile sample	143

List of Tables

Table No.	Title	Page
1.1	Composition of pickling liquor	4
1.2	List of hazardous waste	5
1.3	Standards for wastewater emissions from the steel industry in India and Europe	6
2.1	Different types of binding agents for different types of contaminants	17
2.2	Acid and metals recovery from electroplating and pickling liquor by solvent extractants	27
2.3	Summary of all the possible treatment methods of pickling liquor	36
3.1	Different types of neutralizing agents	54
3.2	Designation of samples with different combination for SPL treatment	56
3.3	Characterization of pickling effluent	62
3.4	Treated SPL parameters	63
3.5	Sludge generated during SPL treatment	65
3.6	Cost of various treatments	66
3.7	Sludge Characterization by XRD	69
3.8	Sludge characterization by XRF	70
3.9	List of materials used in the study	72
3.10	BG-11 medium composition	73
3.11	Parameters of column study	79
3.12	Characteristic parameter of the studied kinetic models and the regression coefficients	88
3.13	Characteristic parameters of the studied isotherm models and the regression coefficients	91
3.14	Experimental parameters of the breakthrough curves and characteristic parameters of the Thomas model and Yoon-Nelson model with their corresponding values of the regression coefficient (r^2).	95
4.1	Pickling sludge characterization	105

4.2	Characterization of Copper tailing	106
4.3	Chemical composition of soil	107
4.4	Height of plant under sun condition	108
4.5	Height of plant under shadow condition	109
4.6	Concentration of metal ions in plants in various treatments	110
4.7	Designation of tiles	115
4.8	Maximum weight to be retained at the completion of sieving	125
4.9	Minimum weight of sample for sieve analysis	125
4.10	Grading of fine aggregates	126
4.11	Coarse aggregate specifications	127
4.12	Pickling sludge characterization	134
4.13	Sieve analysis of pickling sludge	135
4.14	Chemical and physical properties of cement	136
4.15	Sieve analysis results of fine aggregate	137
4.16	Sieve analysis results of coarse aggregate	137
4.17	TCLP (18 h) test results for sludge-concrete mix pavement tiles after 28 days of curing	138
4.18	Block density of sludge-concrete mix pavement tiles	139
4.19	Absorption of sludge-concrete mix pavement tiles	139
4.20	Drying shrinkage of sludge-concrete mix pavement tiles	140
4.21	Compressive strength of sludge-concrete mix pavement tiles after 7 days	141
4.22	Compressive strength of sludge-concrete mix pavement tiles after 28 days	140

SPL	Spent Pickling Liquor
CPCB	Central Pollution Control Board
MoEF	Ministry of Environment and Forest
IPPC	Integrated Pollution Prevention and Control
TEPR	The Environment Protection Amendment Rules
pH	Power of Hydrogen
EPA	Environmental Protection Agency
S/S	Solidification /Stabilization
DD	Diffusion Dialysis
NF	Nano-Filtration
RO	Reverse Osmosis
MD	Membrane Distillation
EC	Electric Conductivity
TDS	Total Dissolved Solids
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
FTIR	Fourier Transform Infra -Red
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
BDL	Below Detectable Limit
CSH	Calcium -Silica- Hydrate

Chapter 1

Introduction

This chapter includes the background and basis behind the study.

1.1 Background

According to the United States Environmental Protection Agency (USEPA), a hazardous waste may be defined as any residue or combination of residues other than radioactive waste which by reason of its chemical reactivity or toxic, corrosive or ignitability causes substantial present or potential hazard to human health or environment either alone or when in contact with other wastes, and which therefore cannot be handled, stored, transported, treated or disposed off without special precautions (Rao, 2013). Ignitability, corrosivity, reactivity, and toxicity can be defined as

- a) **Ignitability:** Wastes that are hazardous due to the ignitability characteristic include liquids with flash points below 60 °C, non-liquids that cause fire through specific conditions, ignitable compressed gases and oxidizers.
- b) **Corrosivity:** Wastes that are hazardous due to the corrosivity characteristic include aqueous wastes with a pH of less than or equal to 2, a pH greater than or equal to 12.5 or based on the liquids ability to corrode steel.
- c) **Reactivity:** Wastes that are hazardous due to the reactivity characteristic may be unstable under normal conditions, may react with water, may give off toxic gases and may be capable of detonation or explosion under normal conditions or when heated.
- d) **Toxicity:** Toxic wastes are harmful or fatal when ingested or absorbed (e.g., wastes containing mercury, lead, DDT, PCBs, etc.). When toxic wastes are disposed of, the toxic constituents may leach from the waste and pollute ground water.

As per information provided by the Central Pollution Control Board (CPCB) of India, there are about 41,523 industries in the country, generating about 6232507 metric tonnes of hazardous waste annually (CPCB, 2016). Annexure A gives the state-wise status of a number of units generating hazardous waste as well as the quantity of waste generated, for recyclable, incinerable and disposable waste types. The percentage of recyclable, incinerable and disposable hazardous waste is depicted in Figure 1.1. The major types of hazardous waste are from electroplating, pickling, galvanizing, pesticides, paint and dye, petroleum, caustic soda, fertilizers, inorganic chemicals and general engineering plants.

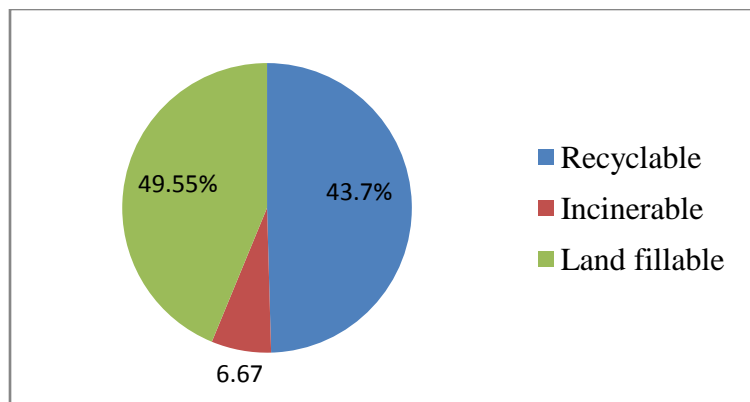


Figure 1.1: Status of hazardous waste generation in India

(Source http://www.cpcb.nic.in/Updated_Inventory_HW_Generation.pdf. Dated 1/4/17)

One of the major hazardous waste comes from pickling plant of the steel industry. Steel finishing operations, such as pickling, galvanizing, plating, etc. involve a surface cleaning process to eliminate the scale, rust, and dust. This process is carried out by immersion of steel in hot acidic solution. Spent baths must be dumped because the efficiency of pickling decreases with increasing content of dissolved metals in the bath. Pickling waste generated in steel streamline is shown in Figure. 1.2 (Rogener et al., 2012).

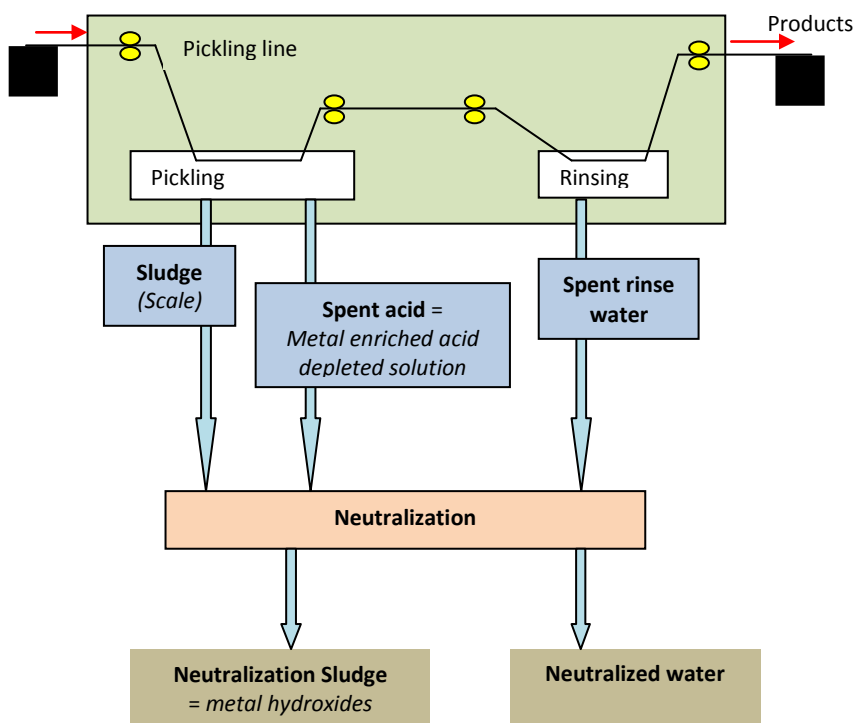


Figure 1.2: Pickling waste generated in the steel streamline (Rogener et al., 2012)

The composition of the pickling bath depends on the composition and thickness of the surface. In general, Spent Pickling Liquor (SPL) can be divided into two groups:

- a) Solutions left after steel pickling in hot-dip galvanizing plants,
- b) Solutions left after stainless steel pickling in rolling mills.

The first group consists of hydrochloric acid, iron and zinc ions (about 5-10% free acid and 5-15% ferrous ions) (Agrawal and Sahu, 2009), whilst the second group contains more harmful acids: a mixture of hydrofluoric and nitric acid or sulfuric acid and its mixture with hydrofluoric acid or hydrogen peroxide, iron and other metal ions. The composition of pickling liquor is given in Table 1.1 (Gálvez et al., 2006). The composition of pickling liquor of stainless steel differs from industry to industry on the basis of requirement of product quality and demand in the market.

Table 1.1: Composition of stainless steel pickling liquor (Gálvez et al., 2006)

Component Composition	(g/l)
Free HNO ₃	100-130
Total NO ₃	120-160
Free HF	20-40
Total F ⁻	60-80
Fe (III)	35-45
Cr (III)	5-10
Ni (II)	3-6

The treatment methods of nitric acid and hydrofluoric acid mixture are better developed than of hydrochloric or sulfuric acid because of the great amount of spend pickling solution generated from stainless steel pickling (Regel- Rosocka et al., 2010). Nevertheless spent pickling solution produced from steel pickling cannot be ignored as it is hazardous in nature (Table 1.2) and has a detrimental effect on the environment. Thus, the focus of this study was to treat pickling liquor generated from mild steel pickling process.

Table 1.2: List of hazardous waste (MoEF Notification- New Delhi, 2016)

Process	Hazardous waste
Metal Surface Treatment (Such as etching, staining, polishing, galvanizing, cleaning, degreasing, plating etc.)	Acid Residues
	Alkali residues
	Spent bath/sludge containing sulphide, cyanide and toxic metals
	Sludge from a bath containing organic solvents.
	Phosphate sludge
	Sludge from staining bath Copper etching residues
	Plating metal sludge
	Chemical sludge from wastewater treatment.

Source: http://www.cpcb.nic.in/HWM_Rules_2016.pdf dated (1/4/17)

1.2 Legislations

Every country has its own discharge standards for wastewater, to prevent the environment from pollution. A comparative table of Indian and European measures for wastewater discharge from the steel industry is presented in Table 1.3 [The Environment Protection Amendment Rules (TEPR), 2009 and Integrated Pollution Prevention and Control (IPPC), 2001]. In Indian standards, the discharge limits of treated effluent are different for inland surface water, public sewers, ground and marine coastal areas, but in European standard discharge, limit are same for all areas. In order to prevent the pollution of the environment and to achieve the permissible effluent discharge limit of 3 mg/l iron and pH of 6-9, such effluent has to be treated by suitable technique before their disposal into river/ water stream.

A lot of sludge is generated during the treatment process of pickling liquor. There are severe problems in its disposal to lined sites (landfills). If the sludge is disposed on land, it may pose

serious consequences. During the rains, all the toxic compounds (leachate) will go into the ground and may pollute soil and groundwater.

Table 1.3: Standards for wastewater emissions from the steel industry in India and Europe (TEPR, 2009) and (IPPC, 2001)

S. No.	Parameter	Indian standard				European Standard
		Inland surface water	Public sewers	Land for irrigation	Marine coastal areas	All areas
1	Suspended solids, (mg/l), max	100	600	200	(a) For process waste water-100	20
					(b) For cooling water effluent 10 percent above total suspended matter of influent	
2	pH Value	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0	6.5 to 8.5
3	Oil and grease (mg/l)	10	20	10	20	5
4	Chemical Oxygen demand (mg/l), max	250	-	-	250	-
5	Hexavalent Chromium, (mg/l), max	0.1	2	-	1	-
6	Total Chromium (mg/l), max	2	2	-	2	0.5
7	Zinc (mg/l), max	5	15	-	15	0.5
8	Nickel (mg/l), max	3	3	-	5	0.5
9	Iron (mg/l), max	3	3	-	3	10

Therefore, an attempt has been made in the present research work to treat the pickling liquor in economic and environmentally friendly method and utilize the pickling sludge.

1.3 Formulation of Problem

The hazardous waste, as its name suggests, is toxic in nature. The management and disposal of hazardous waste require adequate control and proper handling, which is very costly. India had enacted the Hazardous Waste (Management and Handling) amendment Rules 2009, which controls the handling, treatment, and disposal of hazardous waste (MoEF, 2009).

Pickling process is carried out prior to electroplating, galvanizing and metal preparation. In India, there are many galvanizing steel processing plants. In these plants, steel is pickled in sulphuric acid and hydrochloric acid.

Galvanizing is a process undertaken to coat ferrous metals and metal products in a layer of zinc to prolong their life. The metal to be coated requires pre-treatment prior to being immersed in the zinc bath in order to remove rust, grease, and other materials, and therefore to promote the galvanizing process. Pre-treatment can include treatment of the metal with an alkaline degreasing solution, an acid pickling solution, water rinse, and a pre-flux solution. The pre-flux solution is usually comprised of zinc ammonium chloride ($ZnCl_2 \cdot 3NH_4Cl$) and is used to promote the zinc-metal bond. After pre-treatment, the metal is immersed in molten zinc, followed by a quench bath. Figure 1.4 depicts a basic galvanizing flow diagram and likely emission points. Mild steel pickling process is highlighted in Figure 1.4.

Disposal of pickling sludge, as per the Act of Hazardous Waste (Management and Handling) Amendment Rules, 2009 is not an easy task. Its transportation and construction of lined disposal sites involve expenditure, and so some of the sludge is being disposed off on the sides of roads and railway tracks to generally fill the low lying areas. This may cause severe health hazards. Therefore, a study has been attempted to treat pickling liquor in economic and environmentally friendly method.

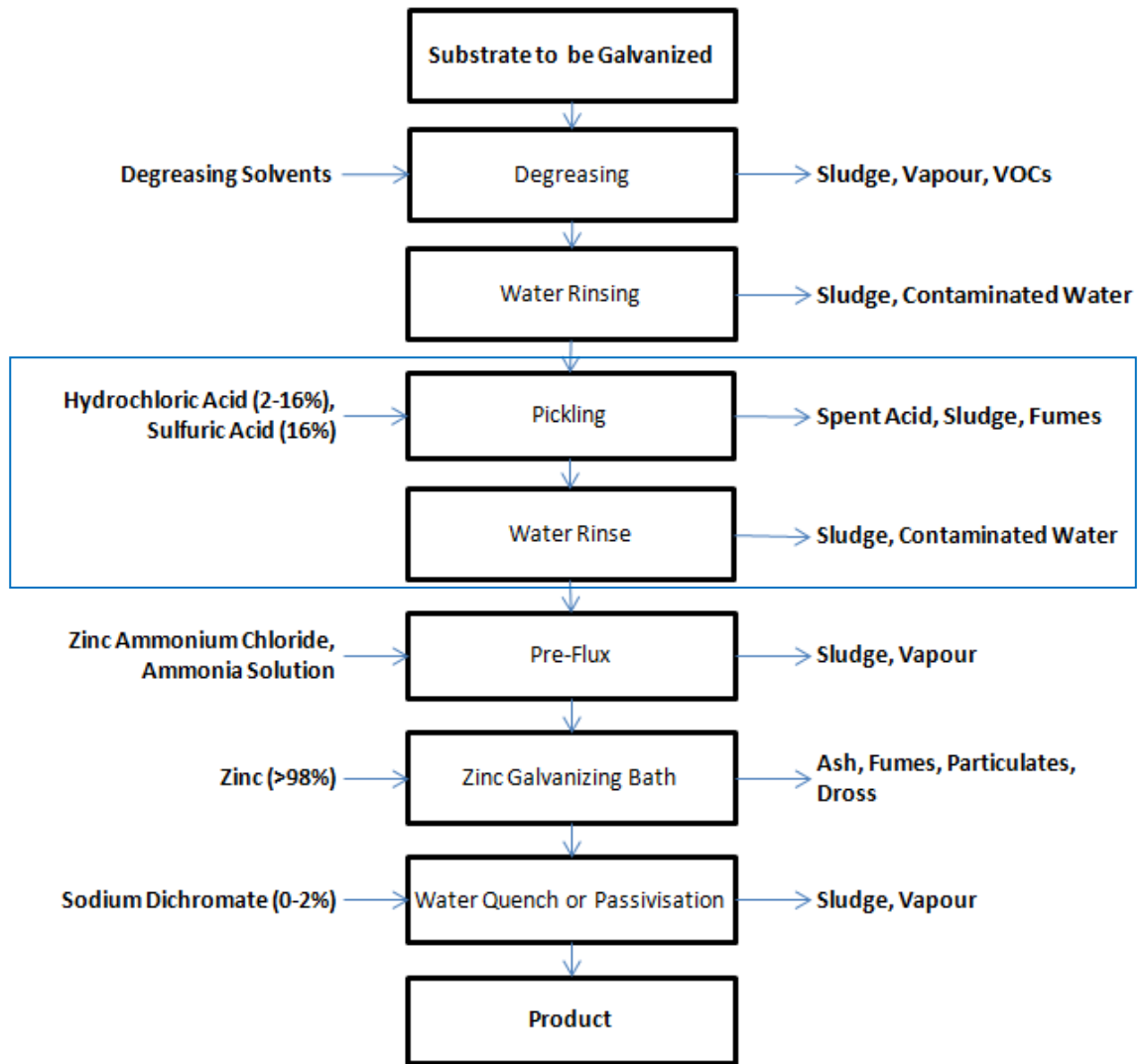


Figure 1.4: The basic galvanizing process steps and likely emission points

In the present research work, samples have been collected from steel industries. These industries are pickling the steel sheets in hydrochloric acid baths. The wastes generated during the pickling process can be classified into the following:

- a) Sludge containing metal oxides generated by the precipitation of metal scale, rust, and dust which settles at the bottom
- b) Sludge containing hydroxides generated during the treatment of the pickling wastewater and spent liquor with lime (Singhal et al., 2007).

The chemical reactions due to pickling process lead to the formation of metal salts and results in significant release of waste products such as metal oxide particles, metal-enriched

acid solutions and metal containing neutralization sludge (Rogener et al., 2012). Due to the presence of high content of residual acid and metals, SPL has been designated as K062 Environmental Protection Agency (EPA) hazardous waste list of the USA (Bing et al., 2012).

Recently, the emphasis has been laid on the regeneration of spend acid in large industries. Two approaches that have been widely in use can be summarized as either total regeneration of acid and metals by Pyro metallurgical processes or partial regeneration of the acid by diffusion dialysis, retardation, nanofiltration or electro dialysis (Regel-Rosocka 2010; Baba et al., 2011). Although these processes significantly reduce the volume of the waste to be discharged, they demand huge investment and pose an environmental risk during transportation (Devi et al., 2014).

The most common technology used for the treatment of the pickling liquor is neutralization with alkaline additives such as caustic soda, liquid ammonia, quicklime, limestone or slaked lime (Ito et al., 1998). Neutralization of the pickling liquor leads to sludge production and thereby necessitates its disposal. Methods such as landfills have been put to use for the disposal of such hazardous materials. However, the landfill technique poses problems like the continuous demand of land, pollution of soil and groundwater due to leaching of heavy metals etc. Solidification/Stabilization (S/S) is one of a technique for disposal of hazardous waste. Various types of binders are used prior to landfill disposal of hazardous waste (Minocha et al. 2003; Wang 2009). The objectives of S/S process are (a) chemically react with the free water in the waste to form a dry solid, and (b) makes the contaminants as immobile as possible. The high leachability of heavy metals in sludge requires proper sludge management, including waste minimization, metal recovery and safe disposal (Vijay, 2003). Singhal et al. in 2006 tried to reduce the generation of sludge during treatment of pickling liquor of stainless steel. Reuse of industrial solid waste as a partial replacement of aggregate in construction activities not only saves landfill space but also reduces the demand for extraction of natural raw materials (Ismail et al., 2008).

Therefore, this study was also undertaken to explore the possibility of utilizing S/S pickling sludge in pavement tiles as a partial replacement of cement.

1.4 Scope and Objectives

Neutralization is the conventional and economic treatment method for the small-scale industries. The method is simple and no complex installation is needed. However, it consumes a lot of chemicals. The precipitate of iron and zinc hydroxides, after sedimentation, is filtered and dumped in a landfill. The main drawback of this process is the storage cost of the sludge. Its transportation and construction of lined disposal sites pose a severe problem. In the normal practice, sludge is being disposed into the low-lying areas. This may contaminate the groundwater. Moreover, no selective recovery of chemicals from the mixture of Fe and Zn hydroxides and neutral salts is possible (Jianzhao et al., 2016). By solidification and stabilization sludge can be safely disposed. But this method is limited by the growing need for landfills to store hazardous waste (Deyi et al. 2015). Evaporation/crystallization and spray roasting require high initial installation cost and energy and it is not amenable to small-scale plant (Grazia, 2016; Sinha et al., 2015). Solvent extraction method has certain advantages and disadvantages. The advantages are (a) it is very flexible and (b) it permits to process effluent over a wide concentration range of metal ion (Agrawal et al., 2011). The disadvantages are (a) emulsion formation, (b) low efficiency, (c) loss of compounds and (d) laborious. Other methods like membrane separation and low-temperature crystallization are costly and highly energy intensive. Treatment of SPL with biosorption is still in the infant stage and a lot of study required in this area because it's a cost-effective treatment method even though for a low concentration of heavy metals.

Moreover, the treatment methods of mixed acid are better recovered than hydrochloric or sulphuric acid because of a large amount of SPL produced from stainless steel pickling. Nevertheless, SPL produces from mild steel pickling cannot be neglected as it is hazardous in nature and has a detrimental effect on the environment. Thus, the focus of this study to treat pickling liquor in economic and environmentally friendly way.

Hence, the aim of the present work is to study on the SPL of mild steel industry with following objectives:

- a) To minimize the generation of sludge during neutralization treatment of spent pickling liquor.

- b) Cost economic study of different treatment methods.
- c) Investigate the feasibility of utilizing sludge as a fertilizer and manufacture of pavement tiles.
- d) Treatment of pickling waste by biosorption methods by using different media and optimization of its process parameter and kinetic study.

References

Agrawal Archana, K.K. Sahu (2009). An overview of the recovery of acid from spent acidic solutions from steel and electroplating industries, *Journal of Hazardous Materials*, 171: 61–75.

Agrawal Archana, Kumari S., Sahu K.K. (2011). Studies on solvent extraction of iron (III) as a step for conversion of a waste effluent to a value added product, *Journal of Environmental Management*, 92(12): 3105–3111.

Baba AA, Adekola FA, Awobode OS, Adekunle BR, Pradhan S, Biswal A (2011). Analysis of heavy metals from spent pickling liquor of sulfuric acid. *International Journal of Chemical*, 21(4): 231–240.

Bing Tang, Wen Su, Jing Wang, Fenglian Fu, Guojun Yu, Jianyin Zhang (2012). Minimizing the creation of spent pickling liquors in a pickling process with high-concentration hydrochloric acid solutions: Mechanism and evaluation method, *Journal of Environmental Management*, 98: 147-154.

Central Pollution Control Board (CPCB 2016) MOEF, India, home page. http://www.cpcb.nic.in/Updated_Inventory_HW_Generation.pdf. Dated 1/4/17

Devi A, Singhal A, Gupta R, Panzade P (2014) A Study on treatment methods of spent pickling liquor generated by pickling process of mild steel *Clean Technologies and Environmental Policy*, 16 (8): 1515-1527.

Deyi Hou, Qingbao Gu, Fujun Ma, Shannon O'Connellc (2016). Life cycle assessment comparison of thermal desorption and stabilization/solidification of mercury contaminated soil on agricultural land, *Journal of Cleaner Production*, 139: 949–956.

Gálvez J.L., Dufour J., Negro C., López-Mateos. F. (2006). Fluoride speciation in stainless steel pickling liquor. *The Iron and Steel Institute of Japan International*, 46(2): 281-286

Grazia Leonzio (2016) Recovery of metal sulphates and hydrochloric acid from spent pickling liquors, *Journal of Cleaner Production*, 129: 417–426.

Integrated Pollution Prevention and Control (IPPC) reference document on best available techniques in the ferrous metals processing industry December 2001 [Online] Available at: ftp://ftp.jrc.es/pub/eippcb/doc/fmp_bref_1201.pdf Dated: 24/4/2014

Ismail ZZ, AL-Hashmi EA (2008). Reuse of waste iron as a partial replacement of sand in concrete. *Waste Management*, 28: 2048–2053.

Ito M, Tachibana R, Fukushima K, Seino Y, Yamamoto A, Kawabata Y (1998). Characteristics and production: mechanism of sulfuric acid and nitric–hydrofluoric acid pickling sludge produced in manufacture of stainless steel. *Journal of Chemical Engineering Japan*, 31: 589–595.

Jianzhao Tang, Yuwen Pei, Qinhai Hu, Dongdong Pei, Junpeng Xu (2016). The recycling of ferric salt in steel pickling liquors: preparation of nano-sized iron oxide, *The Tenth International Conference on Waste Management and Technology (ICWMT) Procedia Environmental Sciences*, 31: 778 – 784.

Minocha AK, Jain N, Verma CL (2003). Effect of inorganic materials on the solidification of heavy metals sludge. *Cement Concrete Resource*, 33: 1695–1701.

Regel- Rosocka M (2010). A review on methods of regeneration of spent pickling solution from steel processing. *Journal of Hazardous Material*, 177: 57-69.

Rogener F, Sartor M, Ban A, Bucholoh D (2012). Metal recovery from spent stainless steel pickling solution. *Resour Conserv Recycl*, 60: 72–77.

Singhal Anupam, Prakash Satya and Tewari V.K. (2006). A study on sludge minimization during the treatment of pickling effluent. *Journal of Environmental Science & Engineering, NEERI, Nagpur, India*, 48(2): 109-112.

Singhal Anupam, Prakash Satya and Tewari V.K. (2007). Trials on sludge of lime treated spent liquor of pickling unit for use in the cement concrete and its leaching characteristics. *Building and Environment*, 42: 196-202.

Sinha Manish K., Sahu Sushanta K., Meshram Pratima, Prasad L.B., Pandey Banshi D.(2015). Low temperature hydrothermal synthesis and characterization of iron oxide powders of diverse morphologies from spent pickle liquor, *Powder Technology*, 276: 214–221.

The Environment Protection Amendment Rules (TEPR) (2009). General Standards for Discharge of Environmental Pollutants Part-A: Effluents [Schedule – VI] : 545-548.

The Gazette of India (2016) Extraordinarily, Part-II, Section 3, Sub-section (i), published by Min. of Environment & Forest, Notification, New Delhi.

The Gazette of India (2009), Extraordinarily, Part-II, Section 3, Sub-section (ii), published by Authority No. 471, Min. of Environment & Forest, Notification, New Delhi.

Vijay R, Sihorwala TA (2003). Identification and leaching characteristics of sludge generated from metal pickling and electroplating industries by toxicity characteristics leaching procedure (TCLP). *Environmental Monitoring and Assessment (Netherlands)*, 84: 193–202

Wang LK (2009). Waste treatment in the metal manufacturing, forming, coating and finishing industries. *Waste Treatment Bulletin*, New York.

Rao CS (2013). *Environmental pollution control engineering*, 2nd edition, New Age International (P) Limited, New Delhi.

Chapter 2

Literature review

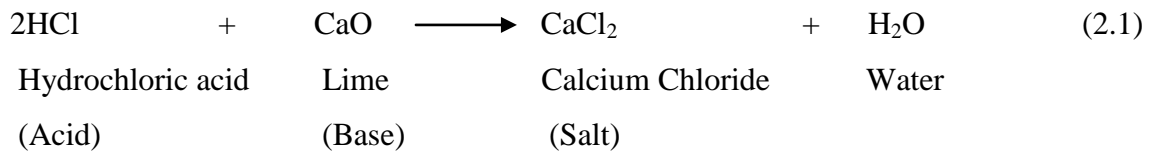
This chapter provides the in-depth literature survey carried out during the research work.

2.1 Introduction

Spent pickling liquor (SPL) is listed as hazardous waste due to its corrosive nature (pH less than 1) and presence of heavy metals. In parliamentary law to prevent the contamination of the surroundings and to achieve the permissible effluent discharge limit, many techniques have been tried for its treatment. Treatment methods can be separated into two category 1) Conventional method includes neutralization followed by safe sludge disposal technique (Solidification /Stabilization) and 2) advance treatment methods include a) recovery and regeneration of metals and acids and b) green method (Biosorption).

2.2 Established Method: Neutralization/ Precipitation

Pickle liquor cannot ordinarily be processed to recover usable by-products profitably. Spent liquor is a relatively dilute solution of low-cost heavy chemicals. Therefore, a most economical method for treatment of SPL is neutralization with lime or some other cheap alkaline agent. The selection of an agent should be based on a) Cost per ton of available basicity b) Space available c) Reaction time d) Pickle liquor volume e) Availability of agent and f) Character of sludge produced.



Pickling liquor can be given complete treatment (precipitation of metals) with lime in a plant by providing efficient agitation and aeration. Various neutralizing agents (soda ash, caustic soda, ammonia, dolomite lime, high calcium lime, pulverized high calcium limestone and dolomite lime precipitated chalk, cement dust, acetylene sludge) can be used for the treatment of SPL but the substantial economy can be obtained by high calcium limestone (Hoak and Lewis, 1948). SPL treatment with limestone and limes varies widely in their rate of reaction with pickle liquor, and the rate depends upon particle size, chemical analysis, and a specific reactivity peculiar to a particular limestone. The rate at which Limestone removes iron from pickle liquor is a function of the rate at which ferrous iron oxidizes (Hoak and Lewis, 1945; 1947). Sludge volume generation can be brought down by maintaining reaction

bath temperature above 750 °C with efficient aeration, which results in a constant rate of reaction in the bath. Moreover, sludge-settling rate subsequently reduced (Hoak and Lewis 1949).

Iron can be removed from spent pickling liquor by raising the pH about 4 to 4.5 which is conducive to the precipitation of iron. The precipitated iron separated out from the spent pickling liquor by filtration. Makeup the treated spent pickling liquor by fresh acid up to the needed concentration and transport back to the operating process (Raymond and Stephen, 2009). Other metals like Nickel, Chromium, and Zinc can also be removed or recovered from spent pickling solution by precipitation method (Forsell and Nilasson, 1974; Mughal et al., 2008). But the presence of one metal precipitation affects the recovery of other metal (Wang et al., 2011). Ito et al. (1998) defined the characteristics of H₂SO₄ sludge (S-sludge) and nitric hydrofluoric acid sludge (NH-sludge) of stainless steel. Slaked lime was added up to an equivalent ratio of 1:4 for neutralization of the S-sludge and the NH-sludge. S-sludge neutralized sample contains Ca(OH)₂, CaSO₄.2H₂O, FeCr₂O₄ and Cr₂O₃ and NH-sludge sample contains FeCr₂O₄, CaF₂, Ca(OH)₂ and Cr₂O₃.

The drawbacks of conventional treatment method are:

- a) Excessive sludge production: According to one estimate (Ozdemir et al., 2006), if the quantity of SPL generated is 2,028 tons per annum, and so the quantity of NaOH (35 weight%) needed for its neutralization would be around 1,298 tons, and the iron hydroxide sludge produced from this process would be about 244 tons.
- b) Slow metal precipitation kinetics,
- c) Inefficient metal removal due to poor settling and aggregation of metal precipitation,
- d) Landfill disposal problem, and
- e) Contaminate groundwater due to leaching properties of heavy metals

2.2.1 Solidification/Stabilization

Most commonly applied technology for hazardous waste is Solidification/Stabilization (S/S) by various types of binders prior to landfill disposal of hazardous waste. Conner and Hoeffner (1998) described the history of S/S technology. The objectives of S/S process: - a)

chemically react with the free water in the waste to form a dry solid, and b) make the contaminants as immobile as possible.

S/S treatability and final performance of treated waste studies can be placed into two groups: physical and chemical tests. The physical test is unconfined compressive strength test and chemical test or leachability test is called *Toxicity Characteristic Leaching Procedure* (TCLP).

Solidification can be accomplished by a chemical reaction between the waste and solidifying reagents or by mechanical processes. Contaminant migration is much restricted by decreasing the surface area exposed to leaching and/or by coating the wastes with low-permeability materials. The combined process of S/S mixes wastes, soils and sludge with treatment agents to immobilize, both physically and chemically, the hazardous constituents in those kernels. Dissimilar cases of binding reagents like Portland cement, Cement Kiln Dust (CKD), Calcium Oxide, Lime Kiln Dust (LKD), Limestone, Fly Ash, Slag, Gypsum, etc. have been considered by various researchers and the list is given in Table 2.1. Organic binding reagents are rarely practiced in commercial scale due to their high price compared to inorganic binders (Hills et al., 1993).

Table 2.1: Different types of binding agents for different types of contaminants

Sample	Contaminants	Additives & Binder Reagents	Reference
Synthetic waste	Mercury	Cement	Lu C.H (1994)
Organic waste	1,2 dichlorobenzene (DCB) Nitrobenzene	Organo clays . Type I Portland cement	Faschan (1996)
Soil	Lead	Cement	Wilk (1995)
Organic waste	Volatile organic compound (VOC)	Portland cement	Owens & Stewart (1996)
Chloro-alkali Plant	Mercury	Commercially available sludge (Treatment agent)	Yang (1993)

Sample	Contaminants	Additives & Binder Reagents	Reference
Electroplating waste	Water soluble cadmium and nickel salt	Portland cement adsorbent (Silica fume, fly ash and activated carbon)	Tamas (1992)
Heavy waste	Chromium Nitrate	Cement	Ivey et al. (1990)
Heavy waste	Cadmium, copper, chromium, nickel, lead and zinc nitrate	Blast Furnace slag, Fly ash, gypsum, hydrated lime and Portland cement	Albino et al. (1996)
Electroplating waste	Chromium	Heat-treated sludge mixture (electroplating sludge + water purification calcium carbonate sludge) and Portland cement	Yang & Kao (1994)
Cadmium and lead salts aqueous	Cadmium and lead hydroxide	Portland cement	Cartledge & Yang (1990)
Soluble chromium waste	Chromium	Slag cement blend, Portland cement and class F fly ash calcium aluminates (reducing agent)	Kindness et al. (1994)
Zinc and lead waste	Zinc and lead	Lime pozzolana and fiber reinforced lime-pozzolana	Debroy (1994)
Lead nitrate solution	Lead	Type I Portland cement and cement, fly ash (equal proportion) mixture	Wang (1996)

Sample	Contaminants	Additives & Binder Reagents	Reference
Chromium-containing waste	Chromium	Portland cement and blended cement containing Granulated, glassy, blast furnace slag	Macias et al. (1995)
Steel foundry Dust	Lead, chromium, cadmium, zinc	Cement and anhydrite (waste material)	Andres et al. (1995)
Electroplating waste	Nickel, chromium	Ordinary Portland cement with superplasticizer	Yang and Chang (1994)
Heavy metal sludge	Cadmium, chromium, mercury, nickel	Portland cement, class F fly ash binder	Roy et al. (1991)
Arsenic compound	Organoarsenic species, arsanic acid, arsenic trioxide, arsenate	Portland cement	Buchler et al. (1996)
Synthetic electroplating sludge	Cadmium, chromium, mercury, nickel	Ordinary Portland cement (Type I)	Roy et al. (1992)
Inorganic waste	Lead, chromium	Latex modified cement system	Daniali (1990)
Industrial wastewater	Heavy metal	Fly ash, cement	Weng et al. (1994)
Sewage sludge containing heavy metals	Copper, zinc, lead	Bentonite/ cement	Katsiote et al. (2008)

Sample	Contaminants	Additives & Binder Reagents	Reference
Industrial brownfield	Copper, lead, zinc, nickel, arsenic	Portland cement, Calcium Aluminates Cement (CAC), and Pozzolanic Cement (PC), Plasticizers Cementol Delta Ekdra (PCDE) and Cementol Antikorodin (PCA), Polypropylene Fibre (PPF), polyoxyethylene-sorbitan monooleate and aqueous acrylic polymer dispersion	Greya & Domen (2011)
Ni waste	Nickel	Various cement paste (ordinary Portland cement/ Kaolin clay)	Esia et al. (2011)
Steel electric furnace waste	Lead, cadmium, chromium, iron, zinc	Portland cement type-1, low-grade MgO	Cubukuoglu & Ouki (2012)
Heavy metal sludge	Nitrate of chromium, nickel, cadmium, and mercury	Portland cement, fly ash, lime	Minocha et al. (2003)
Electroplating sludge	Ni, Cr, Cd, Hg	Ordinary Portland cement, superplasticizer (modified lignosulphonates and sulphonted formaldehyde)	Gorden et al. (1994)
Electroplating sludge	Ni, Cr, Cd, Hg	Ordinary Type I Portland cement, NaOH	Roy (1993)
Electroplating sludge	Ni, Cr, Cd	Alkali-activated pulverized fuel ash (PFA), lime	Asavapisit and Chotklang (2004)

Sample	Contaminants	Additives & Binder Reagents	Reference
Artificial sample	Hg, Pb, Cr, As and Cd	Chemically Bonded Phosphate Ceramic (CBPC)	Hyun and Tia (2017)
Biofuel fly ash	Heavy metals	Portland cement, an alkali activator (Sodium silicate + Sodium hydroxide), and a mixture of the two	Janne et al. (2016)
Lead-acid battery contaminated soil	Pb	Oyster shell powder, sintered magnesia	Zhuo et al. (2015)
Tannery sludge	Cr	Cement	Montañés et al. (2014)
Mine Tailings	Pb and Zn	Portland cement, Potassium dihydrogen phosphate, and ferric chloride hexahydrate	Desogus et al. (2013)
Artificial sample	Pb(II), Cu(II), Cd(II) and Cr(III)	Kaolin/Zeolite based geopolymers	El-Eswed et al. (2015)

Most commonly used a binding agent in S/S is cement or cement with fly ash (Weitzman and Conner, 1989) and its fundamental aspects are discussed by Roy and Cartledge (1997). Macphee and Glasser (1993) examined the interaction of specific waste species and cement system and also looked back and talked about the various facets of waste species-cement interaction. Cheng and Bishop (1992) analyzed the sound structure, physical construction and metal composition of leached cement-based waste forms.

Many researchers tried to utilize the S/S waste instead of disposing of landfill sites. Espinosa and Tenorio (2000) looked into the possibility of partially substituting a raw meal with galvanic sludge in cement production. They used galvanic sludge in the chromium

electroplating process. Differential thermal analysis tests were performed using cement raw meal and mixtures of cement raw meal and dry sludge. The results showed that the galvanic sludge added up to 2.0 % by weight, did not affect the clinkerization process.

Singhal et al. (2007) utilized the treated spent liquor sludge (TSLS) in cement concrete and studied its leaching characteristics. They found out that compressive strength had increased at lower concentrations of sludge in cement, but at higher concentration of sludge, the strength was reduced. At lower concentration, strength was increased due to gypsum and C-S-H gel formation. During the leaching test, Cr and Ni were absent in leachate up to 5% addition of sludge in the cement. Hence, it is safe to use 5% sludge in a concrete mix of the M20 grade. In another study (Singhal et al., 2008a), fly ash is used with cement sludge. The compressive strength (28 days) of the cement-sludge (7.5% TSLS) -fly ash concrete cubes increased to an optimum value by the addition of fly ash as a replacement of cement. The increase in strength was due to the formation of C-S-H. Increase in fly ash beyond 15% in concrete led to decrease in compressive strength of cement concrete cubes due to a reduction in cementitious materials. Heavy metals (Cr and Ni) were absent in leachate tested at 28 days curing of cement-sludge-fly ash concrete blocks. This may be due to the adsorption phenomenon of fly ash as it has a high specific surface area (Singhal et al., 2008b).

Singhal et al. (2012) utilized pickling sludge with fly ash to make Cement concrete hollow cavity bricks. The compressive strength of cement concrete hollow cavity brick was found to increase with the addition of 7.5% TSLS (treated spent liquor sludge) and 15% fly ash as a partial replacement of cement.

Li et al., (2009) used the Electric Arc Furnace (EAF) dust and pickling sludges and reductant coke powder in the smelting process to strengthen the reduction. Smelting reduction process has been widely applied to treat the various stainless wastes and could recover the valuable metals efficiently. The smelting reduction process is complex to operate and difficult to utilize comparing with the S/S (Zhang and Xin, 2011).

The primary drawback of this process is that many people are allergic to heavy metals, and may exhibit skin edema because of contact with the cement wet paste or concrete. A very small quantity of sludge can be used in building material; construction because of heavy

metals present in sludge retarded the properties of the binding material. Hence, disposal of sludge is still a huge problem (Jianli et al., 2010; Wang et al., 2000) as we know that land disposal restrictions are becoming ever increasingly stringent, driven by the technical, regulatory, and political considerations. Moreover, no selective recovery of chemicals from the mixture of Fe and Zn hydroxides and neutral salts is possible. To the largest extent practicable, alternatives to land disposal are desirable, such as waste minimization, recycling, regeneration and recovery methods.

The disposal of acidic waste by subsurface injection is one of the alternatives for recycling, neutralization, or disposal of land. In the United States, several controlled disposal wells are in use. The EPA banned untreated hazardous waste from the injection unless it is shown that the dissipation will not migrate from the injection zone, or that the hazardous waste will react to make a nonhazardous waste. Particularly if the reaction between acid and rock produces harmless products, underground injection is a sound waste-handling technique. But the disadvantage is to identify such area in the hugely populated country like India. Moreover, the price of transportation of waste acid from plant to disposal area is another problem (Graaff et al., 1998).

2.3 Recovery of Metals and Acid

Recovery of metals and acids is a vital problem not only from the viewpoint of environmental protection but also from that of the economy. Different physicochemical methods have been investigated for acid recovery (such as membrane distillation, diffusion dialysis, evaporation or spray roasting) alone and metal and acid recovery (solvent extraction, membrane separation crystallization) both.

2.3.1 Evaporation and crystallization

There are three ways of getting free acid from *evaporation and crystallization*

- a) Copperas recovery: The waste liquor is heated with scrap iron to neutralize acid either in atmospheric evaporation (Stevenson, 1924) or vacuum evaporation (Mantius, 1938) and the makeup acid is added to the SPL prior to crystallization. This reduces the solubility of ferrous sulphate and increases the efficiency of copperas recovery.

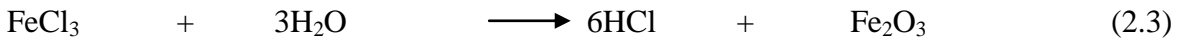
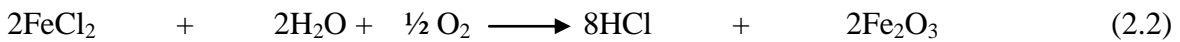
- b) Ferrous sulphate monohydrate: The SPL evaporates directly in a rotary dryer, spray dryer or vacuum evaporation until the sulphuric acid concentration reaches approximately 78%, where ferrous sulphate monohydrate become completely insoluble. Afterward that, monohydrate ferrous sulphate, filtered without reducing the temperature and pressure (Whetzel and Zimmerman, 1935).
- c) Ferric chloride: Pickle liquor containing ferrous chloride and fortified with sufficient HCl is converted to ferric chloride in the presence of oxygen in a tower at a temperature above 50 °C. The oxygen is introduced at the bottom of the tower and ferrous chloride at the top of the tower. The ferric chloride solution from the tower is subject to evaporation so as to increase the concentration of the ferric chloride. The resultant concentrate is recycled back into the tower until a concentration of approximately 40% by weight ferric chloride obtained (Temyanko, 2003).

The problems with evaporation and crystallization process are listed beneath:

- a) Copperas and ferrous monohydrate recovery offer little promise as a general solution of the problem because of a limited market for the compound.
- b) The evaporation and condensation process is very energy intensive and it is not amenable to small-scale plant.

2.3.2 Pyrohydrolysis

Pyrohydrolysis of hydrochloric acid from carbon steel pickling lines is a hydrometallurgical reaction which takes place according to the following chemical reaction.



The water and free acid components included in the initial solution rapidly evaporate at the temperature of the reaction. The roasting gas thus contains the entire free and bonded acid in a form that can be absorbed. The spray roasts process work at a temperature below the sintering temperature of iron oxide. Then, the iron oxide is obtained as a reddish powder. Waste acid roasted in a fluidized bed operates at a higher temperature, which sinters the oxide forming granules (Albert et al., 1999; Barhold and Engelhardt 2001). Iron oxide can be brought down to iron using a partially combusted fuel as a reducing agent (Winter et al.,

2009). The flow sheet diagram of spray roasting process for SPL regeneration is given in Figure 2.1.

The reaction temperature of the process can be reduced by feeding hematite and a reducing agent into a reactor under pressure to form a mechanical bed by maintaining a particular speed of rotation within a reactor and reducing the pressure (Di, 2011). The quality of iron oxide mainly depends on the temperature and flow rate. The contents of Fe, Si, and Mn in the iron oxide are affected by the contents of the respective species in the feed liquor, which in turn depends on the type of steel treated in the pickling line (Ferreira and Mansur, 2011).

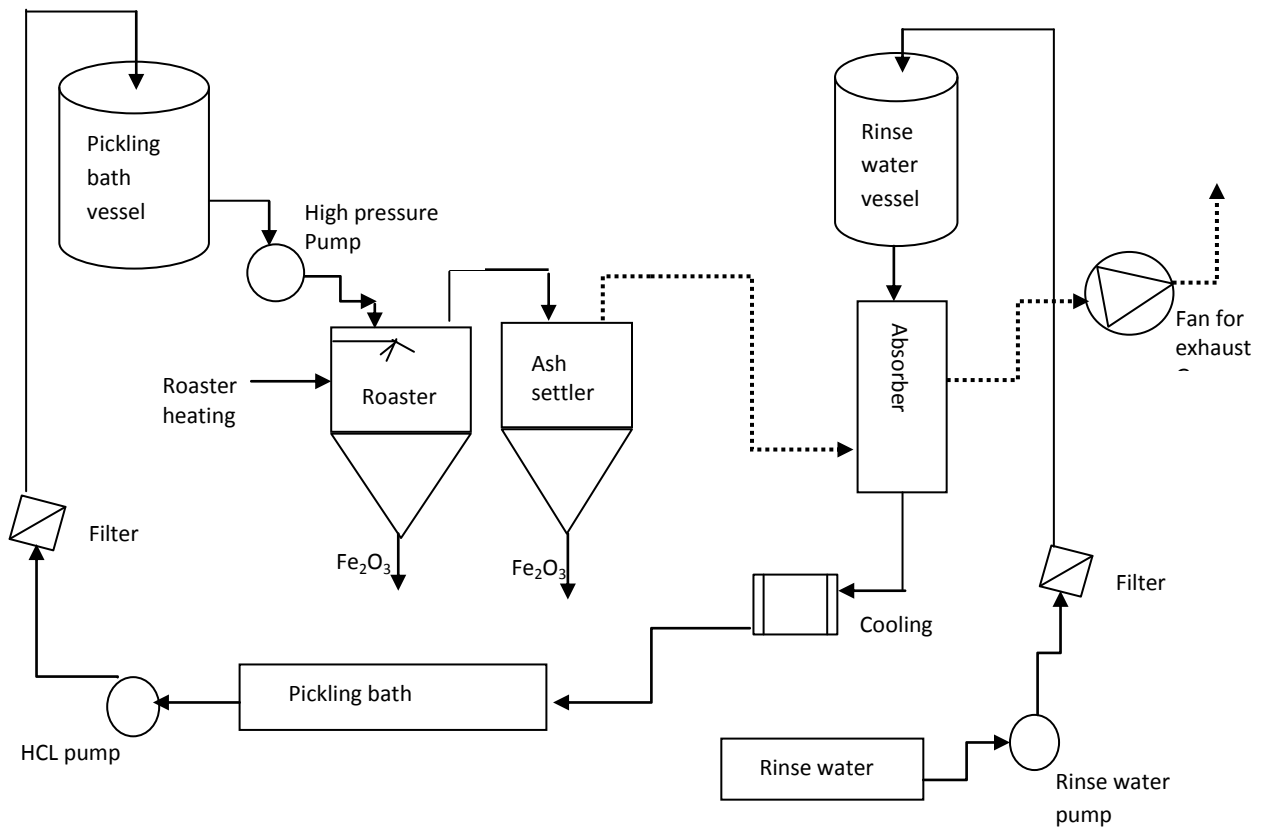


Figure 2.1: Scheme of spray roasting process for SPL regeneration (Di, 2011)

There are a couple of drawbacks to this process:

- a) The market value of iron oxide has been minimal due to the replacement of magnetic recording tapes by other memory media such as CDs.
- b) The Pyro-hydrolysis process is really energy intensive and expensive (energy consumption ranges between 600 and 1200 Kcal/l) (Demopoulos et al., 2008)

- c) The regeneration plant is enormously maintenance intensive due to the extremely corrosive nature of the liquor at elevated operating temperatures.
- d) These operations create a considerable quantity of stack emissions containing HCl, particles, chlorine, which has gone to numerous violation of the U.S cleaner act.

2.3.3 Solvent extraction (SX)

The SX is a process of transfer of soluble metal compounds occurring between aqueous and organic phase, in the liquid multi-component two-phase system. *Extraction* is a chemical reaction between extracted metal ion existing in the aqueous phase and extractant from the organic phase. It enables extraction of valuable metals from pregnant leach solutions (PLS) and acquisition of concentrated and purified solutions directed afterward to appropriate unit operations (electrowinning, crystallization or precipitation of hard-soluble compounds). The SX can be classed as:

- a) Basic extractants (Quaternary and tertiary amine)
- b) Neutral extractants (tri-n-octyl phosphine oxide (TOPO) and tri-n-butyl phosphate (TBP))
- c) Acidic extractants (bis/2,4,4-trimethylpentyl/ phosphinic acid (CYANEX 272), di-(2-ethylhexyl) phosphoric acid (DEHPA) and 2-hydroxy-5-nonylacetophenone oxime (LIX-84))

Acid and metals recovery from electroplating and pickling liquor by using various solvent extractants are listed in Table 2.2.

Fe (III) has been extracted by using CYANEX 923 (trialkylphosphine -TROP) in xylene from hydrochloric acid solutions. CYANEX 923 is a mixture of four trialkylphosphine oxides and it is completely mixable with all commonly used hydrocarbons. The 100% stripping efficiency of Fe (III) achieved by 0.4M Hydrochloric acid in two counter-current levels at an aqueous: organic phase ratio of 3:1 (Saji, 1998). In another work, iron, and acid (sulphuric acid) both recovered from spend pickling solution by using CYANEX 923 with an aqueous: organic phase of 4/1 for 74% acid extraction (Agrawal and Sahu, 2009). A comparative work has been done for Iron (III) extraction from hydrochloric acid leach liquor using Tri-n-butyl phosphate (TBP), CYANEX 923 and CYANEX 921 in distilled kerosene.

The stripping percentage of Fe from the loaded CYANEX 923 has least amongst them (Mishra et al., 2010).

Table 2.2: Acid and metals recovery from electroplating and pickling liquor by solvent extractants

Extractants	Solvent Extractants	Reference
Acid	HCl extraction by CYANEX 921, 923, 925	Heckley et al. (2000)
	H ₂ SO ₄ , HNO ₃ , HCl recovery from electroplating, pickling acids, and diluted acids with CYANEX 923	Chen et al. (1999); Diaz et al. (1999); Da Silva et al. (1999)
Chromium	Extraction with Alamine 336 from industrial plating waste	Sze et al. (1999)
	Cr from ground water with Aliquat 336	Sahu et al. (2008)
	Cr from electroplating with TBP	Gupta et al. (2002)
	Cr and Ni from industrial waste by CYANEX 923	Tanaka et al. (2003)
Cobalt and Nickel	Co and Ni separation from HCl with CYANEX 923 from spent catalysts	Caron et al. (2002)
	Ni from plating baths with LIX 84I	Chimenos et al. (1999)
Copper	Cu from pickling baths with CYANEX 302+ LIX, 860	Rosinda et al. (2002)
	Cu from ammonical etch solution with LIX 84	Benedetto et al. (2001)
	Cu from leach liquor with the extractants LIX 84-I and LIX 622N in kerosene	Panigrahi et al. (2009)
Iron	Fe and Zn with PC88A and DEHPA;	Reddy et al. (2002)
	Fe and In from zinc residues; H ₂ SO ₄ and Fe and Ni from pickling bath	
	Fe, Ti, and V recovery from waste chloride liquors with TBP + EHPA	Agrawal et al. (2011)
	Recovery of Fe by CYANEX 923 from pickling	Regel-Rosocka et al. (2002)
Zinc	Zn from chloride solution with TBP	Alguacil et al. (2001)
	Zn (II) by CYANEX 923	Duche et al. (2002)
Mercury, Zinc and Cobalt	Polyethylene glycol	Hamta and Dehghani (2017)

Extractants	Solvent Extractants	Reference
Arsenic, Copper, Lead, and Zinc	Dithionite and EDTA	Eun et al.(2016)
Rare earth metals	Rare earth from aqueous solutions with Poly(ethylene glycol) functionalized ionic liquids	Xiaojia et al. (2017)
	Rare earth from chloride solution with saponified PC88A	Chan et al. (2016)
Manganese	Mn(II) from a leached liquor with DEHPA and Cyanex 272	Roberto et al. (2012)

Quantitative extraction of Fe (III) has been achieved by using di(2-ethylhexyl)phosphoric acid (DEHPA) mixed with kerosene at phase ratio= 2 in five cross-current stages (El-Nadi and El-Hefny 2010). A model has been developed for predicting the extraction of water and up to 16 M hydrochloric acid by undiluted TBP or TBP diluted with an aliphatic solvent. The model offers the foundation work from which accurate modeling of metal extraction from HCl solution can be progressed (Lum et al., 2012).

Zinc recovery from hydrochloric acid spent pickling liquor has been examined with various solvent extractants. TBP has been selected as one of the suitable extractants. It permits both Zn extraction and the stripping from the loading organic phase with water. But the drawback is that the oxidation of iron also takes place during extraction. CYANEX reagents and ALAMINE 336 (N, N-dioctyloctan-1-amine) extracted zinc strongly, but the stripping with water is ineffective. Moreover, a significant oxidation of iron occurred during the operation. CYANEX 302 is inactive both for zinc and iron and could not be used for extraction from spent pickling solution (Jha et al., 2002). A mathematical model has been developed for forecasting both the extraction and stripping processes for aqueous zinc and acid concentration up to 1.6 and 1mol /l respectively by using TBP diluted in an aliphatic solvent (Lum et al., 2013).

The problem with basic extractants (e.g. ALAMINE 336) is that they form an emulsion in contact with the strong acid solution (Spent pickling solution containing sulphuric acid). The

use of TBP leads to the third phase formation and high concentration is needed to strip Fe (III) from the acidic extractants such as DEHPA.

The drawback of solvent extraction is that there is some confusion related to the extracted metals from a solution of high concentration. The confusion arises from the variety of extracted metals and also the condition at which these metals are determined.

None of the solvent extracting regeneration plants of spent pickling solution is still working. Solvent extraction is not an economically attractive enough to recover zinc from a secondary resource (Jha et al., 2001). However, solvent extraction has great advantages over other methods: it is very flexible, and it permits to process effluent over a wide concentration range of metal ion.

2.3.4 Low-temperature crystallization

The crystallization process operates at low temperatures. Hence, minimizes corrosion and allows the use of inexpensive plastics for piping and other equipment.

Peterson and Salof (1991) patented the processes and apparatus for the closed-loop regeneration of the SPL that had been used to pickle ferrous metals by recovering ferrous chloride from the SPL at very low temperature.

A new process called Pickling Hydrochloric Acid Regeneration had been developed for the regeneration of spent hydrochloric acid pickle liquors by Green technology group (Blumenschein and Olsen, 2003) and its layout is given in Figure 2.2. Sulphuric acid is added to the ferrous chloride-bearing spent HCl pickle liquor. Then the temperature is reduced to below 0 °C, resulting in the crystallization of ferrous sulphate hepta-hydrate and liberation of free hydrochloric acid. Depending upon the crystallization temperature, variable concentrations of sulphate are left in the regenerated acid.

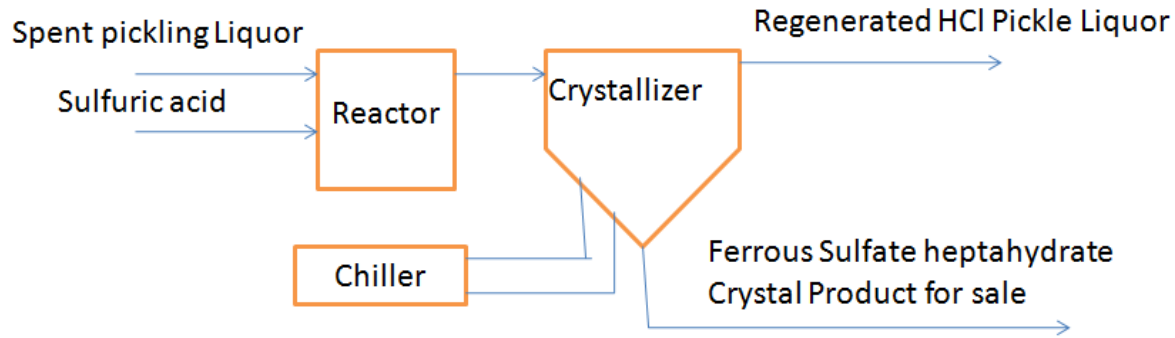


Figure 2.2: Pickling hydrochloric acid regeneration layout (Blumenschein and Olsen, 2003)

Crystallization process requires low energy compared to evaporation process, but the process conditions are not easy to apply since the process requires very low temperature for the crystallization, if very low FeCl_2 and ferrous sulfate hepta-hydrate solubility is desired. Ferrous sulphate hepta-hydrate crystallization modeling has been developed to use framework for parameter estimation for growth and nucleation kinetics and for simulation of batch crystallization process (Shaikh et al., 2013).

Disadvantages may include high energy consumption for the acid evaporation or sludge concentration, difficulties with acids separation and with product washing. Moreover, an economical method for treating the crystal removal is not present and also dead-load of sulphate had an impact on the pickling characteristics of the regenerated acid. By low-temperature crystallization, not the only valuable product can be obtained, but acid can also be regenerated.

2.3.5 Membrane separation

The membrane is a physical barrier that allows certain compounds to pass through, depending on their physical and/or chemical properties. Membranes commonly consist of a porous support layer with a thin dense layer on top that forms the actual membrane. The membranes separation process is extensively used in both water and wastewater treatment because of the following advantages (Zhou and Smith 2002; Scholz and Lucas, 2003)

- a) No chemical addition
- b) A small amount of solids requiring disposal
- c) Very compact installations
- d) Simpler automation and control, and

e) Reduced operation and maintenance requirements

Recovery of metallic ions and acid regeneration by advance membrane separation methods are discussed below:

2.3.5.1 Reverse Osmosis (RO) and Nano-Filtration (NF)

It can recover metallic ions, but they are still expensive due to high energy needs because of the high trans-membranes pressure required (Bernata et al., 2008). The drawbacks of membrane separation process are membrane fouling, insufficient separation, treatment of concentrates, membrane lifetime and chemical resistance and insufficient rejection for individual compounds (Bruggena et al., 2008).

2.3.5.2 Diffusion dialysis

Dialysis is the separation of molecules due to the differences in the rate of movement of the molecules through a semi-permeable barrier. In the recovery of acids with diffusion dialysis (DD), an anion exchange membrane acts as a semi-permeable barrier placed between a running water stream and a flowing acid with a dissolved metal solution.

Some common applications of DD include the recovery of mixed acids of stainless steel pickling baths, recovery of sulphuric acid/hydrochloric acid or sulphuric acid/nitric acid of pickling plants for non-ferrous metals such as zinc and aluminium, recovery of sulphuric acid and hydrochloric acid on steel and non-ferrous pickling baths, hydrochloric acid and nitric acid rack strips, and sulphuric acid anodizing solutions (Cushnie et al., 1994; Oh et al., 2000; Stachera et al., 1998; Bailey et al., 1998; Bailey and Howard 1992). Using pilot scale diffusion dialysis equipment from Pure Cycle Environmental Technologies, Inc., Freshour and Thornton found good nitric acid recovery and iron and nickel rejection, but relatively poor phosphoric acid recovery and titanium rejection (Freshour et al., 2001).

Anion exchange membrane dialysis for acid recovery is potentially applicable to a wide variety of acid-metal salt combinations, but in some cases metal rejection can be limited by metal complexation with the unions that are present in the solutions.

2.3.5.3 Membrane distillation

Membrane distillation (MD) is the procedure where a hydrophobic, micro-porous membrane separates two aqueous solutions by the partial pressure difference caused by the temperature gradient in both positions of the membrane (Lawson and Lloyd, 1997). In the recovery of HCl, the presence of FeCl₃ results in a high molar flux of HCl through the membrane and enhanced the separation of HCl from the salt (Tomaszewska et al., 1998). The fouling of the membranes and concentration and temperature polarization limits MD application. Moreover, MD is a more expensive method than DD. Although DD has a number of advantages: low energy consumption, low installation and operating cost; stable, reliable and easy operation and no pollution to the environment, but it has many drawbacks, also: low processing capability and efficiency, incomplete recovery of acids from the feed, loss of metals, less effective for lower concentration feed or feed with solid particles. To overcome these problems, DD is integrated with other methods like electro dialysis, Ion exchange membrane-electro wining, vacuum membrane distillation and ceramic membrane micro filtration (Luo et al., 2011).

2.3.5.4 Other treatments options

- a) Hydrolyzed aluminum dross odour problems can be prevented by stabilizing aluminum dross through the addition of aqueous ferrous chloride (Spent pickling liquor). Hydrolyzed aluminum dross reacts with ferrous chloride and forms a stabilized compound, which is suitable for sanitary landfill. This resolves the temporary dross storage, bad odour, and safety issues related to the burial of waste (Liu and Chou, 2013).
- b) Oil-based Fe-Co magnetic fluid manufactured by oxidation of Fe (II) of spent pickling liquor (Zorigtkhuu et al., 2006).
- c) Fe₃O₄/ZnCr layered double hydroxide adsorbent via a two-step microwave hydrothermal method with electroplating wastewater and spent pickling liquor for removal of heavy metal from dyes effluent (Dan et al., 2012).
- d) Mn–Zn ferrite powder, made by using oxides of manganese and zinc extracted from used dry batteries, and ferrous chloride solution from waste steel pickling liquor via

- the hydrothermal process. Mn–Zn ferrite powder is primarily used as cores for inductors, transformers, recording heads and noise filters (Liu et al., 2007).
- e) Ni–Cu–Zn ferrite powder synthesized by using the steel pickling liquor and the waste solution of electroplating via the hydrothermal process. Ni–Cu–Zn ferrite is usually used as a magnetic material for Multilayer chip inductors (one of the important components for electronics products, such as cellular phones, notebook computers, video cameras, etc.) due to its lower sintering temperature and better properties at a high frequency (Fu et al., 2006).
 - f) Ferrite synthesized from pickling liquor and the waste solution of electroplating via microwave hydrothermal process and also heavy metals contamination eliminated from the spent pickling liquor. Ferrite is an important electronic material (Chen et al., 2011; Ciminelli et al. 2006).
 - g) Ferrous ferrite nano-sized magnetic particles with the super - paramagnetism property have been prepared from spent pickling liquor by ultrasonic-assisted chemical co-precipitated method (Tang et al., 2009).
 - h) Synthesis of manganese, zinc ferrite by utilizing hydrochloric acid-based SPL and medium-grade pyrolusite ore by precipitation method. Manganese-zinc ferrite is an important soft magnetic material that possesses high magnetic permeabilities and low magnetic core losses. It is widely applied in many electronic and magnetic applications such as inductors, AC/DC converters, wideband transformers, noise filters etc. (Narasimhan, et al., 2011).

These methods are extensively costly and can be utilized for a small quantity of spend pickling liquor. These methods have been tested in laboratory scale and no any commercial installation.

Till now, various treatment methods are discussed and these methods are required either huge quantity of chemicals or energy. Thus, the research community has acquired their interest in a new approach to the treatment of SPL i.e Bioremediation. Bioremediation is a green method which has been proven as more efficient and economical for treatment of industrial effluent. Bioremediation can be defined as a waste management technique that involves the use of organisms to remove or neutralize pollutants from a contaminated site. Methods used

for bioremediation of industrial effluent are either biosorption or bioaccumulation. The most frequently used bioremediators are bacteria, fungi, algae, and yeasts. The major advantages of biosorption/bioaccumulation over other treatment methods include Low cost; High efficiency; Minimization of chemicals; No additional nutrient requirement; Regeneration of absorbent; Possibility of metal recovery & No sludge generation.

2.4 Biosorption

Biosorption is a metabolically passive process, means it does not require energy, and the amount of contaminants a sorbent can remove is dependent on kinetic equilibrium and the composition of the sorbents cellular surface. Contaminants are adsorbed onto the cellular structure (Vijayaraghavan and Yun, 2008; Palmer, 1969). The biosorbents have been categorized under microorganism like bacteria, fungi, yeast, algae, agricultural by-products like rice husk, bran of rice, wheat, sugarcane bagasse, fruit wastes, weeds etc. and other polysaccharide materials. The biosorbents, irrespective of their source have demonstrated good metal removal efficiencies (Gülay et al., 2009; Sisca et al., 2009; Ahalya et al., 2003). The microbial biosorbents have been either cultured or developed in the laboratory. Potential bacterial biosorbents showing good metal removal capacities have been identified as gram-positive bacteria (*Bacillus*, *Corynebacterium*, *Streptomyces*, *Staphylococcus* sp., etc.), gram-negative bacteria (*Enterobacter*, *Aeromonas* sp., *Pseudomonas* etc.) and a cyanobacterium (*Anabaena* sp., etc.) (Gupta Vinod et al., 2015). Fungal biosorbents which include yeast (*Penicillium*, *Saccharomyces*), molds (*Aspergillus*, *Rhizopus*) and mushrooms have shown the lowest biosorption potential (Salman et al., 2014). Various species of red algae (*Gelidium*), blue-green algae (*Nostoc*, *Spirulina* sp., etc.), green (*Ulva*, *Oedogonium* sp., etc.) and brown algae (*Cystoseira*, *Sargassum* sp., etc.) (Geoffrey, 2009) have also been used as efficient biosorbents. Margaryan (2012) has isolated 25 mesophilic and thermophile metal-tolerant bacilli from soil and silt samples to accumulate the nickel, zinc, chromate, cobalt, molybdenum, and copper (Lopez et al., 1997). Some complexing agents (CAs) increase the efficiency of biosorption in the removal of heavy metals (Margaryan 2012).

The factors affect the biosorption process are temperature, pH, biomass concentration and metal concentration in the solution (Marta et al. 2012). Lopez et al. (2012), has done

laboratory - scale studies of the bacteriological treatment of spent sulfuric acid of the pickling process in the steel industry. A strain of *Thiobacillus ferrooxidans* was successfully subcultured in order to adjust it to different pH and dilutions of initial SPL. Once adjusted, the bacteria were able to oxidize all ferrous ions in the diluted sulfuric water residues, making iron and ammonium sulfates. By evaporation/crystallization and later calcinations at temperatures between 800 – 1000 °C, hematite was obtained. The process produced 50 kg of Fe₂O₃ per m³ of waste pickling liquor with 99.8% weight iron recovery (Safari et al., 2012). Iron and manganese adsorption with rice husk ash has been studied (Adekola et al., 2016). Very few publications have been reported related to bioremediation of pickling liquor.

2.5 Research Gaps

Spent pickling liquor is identified as a hazardous waste as per Indian standard (MoEF, 2009). Thus, it should be treated before release or dispose into the river or land. A summary of all the possible treatment methods is presented in Table 2.3. Neutralization is the conventional and economic treatment method for the small-scale industries. The method is simple and no complex installation is needed. It consumes chemicals and generates a lot of sludge. The pickling sludge is being disposed into the low-lying area without proper treatment. This causes a severe problem because, during rains, the entire toxic compound (leachate) goes into the ground and pollutes the groundwater. S/S is a safe disposal method; nevertheless, it is limited by the growing demand for landfills to store the processed sludge. Evaporation/crystallization and spray roasting require high initial installation cost and energy, and it is not amenable to small-scale plant. Solvent extraction method has certain advantages and disadvantages. The advantages are (a) it is very flexible and (b) it permits to process effluent over the wide concentration range of metals ion. The disadvantages are (a) emulsion formation, (b) low efficiency, (c) loss of compounds and (d) laborious. Other methods like membrane separation and low-temperature crystallization are costly and high energy intensive and not amenable to the small-scale industries. Biosorption method has major advantages over other treatment methods include: high efficiency; low cost; minimization of chemicals; regeneration of absorbent; no additional nutrient requirement; possibility of metal recovery & no sludge generation. Treatment of SPL with biosorption is still in the infant stage and an extensive research is required in this field because it's a cost-

effective treatment method even though for a low concentration of heavy metals. The treatment and recovery methods of SPL generated by stainless steel are well developed and studied. Nevertheless, the SPL generated from mild steel cannot be ignored.

Hence, keeping these research gaps in mind, a study has been undertaken to treat the SPL by an economic and environmentally friendly method, minimize the generation of sludge during the treatment process and utilize it for some commercial product to reduce the burden of sludge disposal.

Table 2.3: Summary of all the possible treatment methods of pickling liquor

Possible methods for treatment of pickling liquor	End products	Disadvantages
Neutralization	Large volume of Sludge Production	Sludge disposal problem
Solidification and Stabilization	Safe disposal	Large landfill site required
Evaporation and crystallization	Copperas and ferrous sulphate monohydrate	Limited market, energy intensive
Pyrohydrolysis	HCl and Fe ₂ O ₃	Produce a considerable amount of stack emissions containing HCl, particles, chlorine
Solvent Extraction (SX)	Recovery of HCl, Fe, and Zn by organic solvent e.g. HCl extraction by Cyanex 921, 923, 925	Emulsion formation, low efficiency, loss of compounds and laborious
Low-temperature crystallization	HCl and ferrous sulfate heptahydrate	Conditions are not easy to apply since the process requires very low temperature for the crystallization
Membrane separation (eg. RO, NF, DD, MD)	HCl, Fe, and Zn	Expensive, fouling of the membranes
Biosorption	Heavy metals free acid	Disposal of exhaust biomass

References

- Adekola F. A., Hodonou D. S. S., Adegoke H. I. (2016). Thermodynamic and kinetic studies of biosorption of iron and manganese from aqueous medium using rice husk ash. *Applied Water Science*, 6(4): 319–330.
- Agrawal A, Kumari S, Sahu KK (2011). Studies on solvent extraction of Fe (III) as a step conversion of a waste effluent to a value added product. *Journal of environmental management*, 92: 3105-3111.
- Agrawal A, Sahu KK (2009). Value addition to sulfate waste pickle liquor of steel industry using hydro metallurgical processes. *Metallurgical and Materials Transactions, B* 40: 877-885.
- Ahalya N., Ramachandra T.V. and Kanamadi R.D. (2003). Biosorption of heavy metals. *Research Journal of Chemistry and Environment*, 7(4): 71-79.
- Albert Labl (1999). Process and Plant for extraction or recovery of acid from solution of these acids. U S Patent 5980850.
- Albino V, Cioffi R, De VB, and Santoro L (1996). evaluation of solid waste stabilization processes by means of leaching tests. *Environmental Technology*, 17: 309-315.
- Alguacil J F, Susana M (2001). Solvent extraction of Zn (II) by Cyanex 923 and its application to a solid-supported liquid membrane system. *Journal of Chemical technology and Biotechnology*, 76: 298-302
- Andres A, Ortiz I, Viguri JR, Irabien A (1995). Long-term behaviour of toxic metals in stabilized steel foundry dusts. *Journal of Hazardous Materials*, 40: 31-42.
- Asavapisit S, Chotklang D (2004). Solidification of electroplating sludge using alkali-activated pulverized fuel ash as cementitious binder. *Cement and Concrete Research*, 34(2): 349–353.
- Bailey DE (1998). Optimizing anodizing baths with diffusion dialysis. *Metal Finishing*, 96: 14-17.

- Bailey DE, Howard T (1992). Acid recovery with diffusion dialysis. *Metal Finishing*, 90: 21-23.
- Barhold F, Engelhardt W (2002). Method of regenerating a spent pickling solution. U S Patent 6375915.
- Benedetto J, Morais CA (2001). Proceedings of VI Southern Hemisphere Meeting on Mineral Technology, Rio de Janeiro. CETEM/MCT: 410-415.
- Bernata X (2008). Recovery of Iron (III) from aqueous stream by ultra filtration. *Desalination*, 221: 413-418.
- Blumenschein CD, Olsen DR (2003). Regenerating Spent Pickling Liquor. US patent 20030026746.
- Bruggena BV, Manttari M, Nystromb M (2008). Drawbacks of applying nanofiltration and how to avoid them: A review. *Separation and Purification Technology*, 63: 251-263.
- Buchler P, Hanna R, Akhter H, Cartledge F, Tittlebaum M (1996). Solidification /Stabilization of arsenic speciation. *J. Environ. Sci. Health, A 31 (4): 747-754.*
- Caron L, Stambouli M, Durand G (2002). Proceedings of International Solvent extraction Conference'02. Cape Town, South Africa: 774-780.
- Cartledge FK, Yang SL (1990). Immobilization mechanisms in solidification/stabilization of cadmium and lead salts using portland cement fixing agents. *Environmental Science and Technology*, 24: 867-873.
- Chen D, Fei W, Pratt HRC, Stevens GW (1999). Proceedings of International Solvent extraction Conference'99. Barcelona, Spain, Pub. Society Chemical Industry, London: 469-473.
- Chen D, Li Y, Zhanga J, Li W, Zhou J, Shao L, Qian G (2012). Efficient removal of dyes by a novel magnetic Fe₃O₄/ZnCr-layered double hydroxide adsorbent from heavy metal wastewater. *Journal of Hazardous Materials*, 243: 152-160.

Chen D, Mei CY, Yao LH, Jin HM, Qian GR, Xu ZP (2011). Flash fixation of heavy metals from two industrial wastes into ferrite by microwave hydrothermal co-treatment. *Journal of Hazardous Materials*, 192: 1675– 1682.

Cheng KY, Bishop P (1992). Metals distribution in solidified/stabilized waste forms after leaching. *Hazardous Waste and Hazardous Materials*, 9: 163-171.

Chimenos JM, Fernandez MA, Segarra M, Fernandez AI, Esparducer A, Espiell F (1999). *Proceedings of International Solvent extraction Conference'99*. Barcelona, Spain, Pub. Society Chemical Industry, London: 759-764.

Ciminelli VST, Dias A, Braga HC (2006). Simultaneous production of impurity-free water and magnetite from steel pickling liquors by microwave-hydrothermal processing. *Hydrometallurgy*, 84: 37–42.

Conner JR, Hoeffner SL (1998). *The History of Stabilization/Solidification Technology*. *Critical Reviews in Environmental Science and Technology*, 28: 325-396.

Cubukcuoglu B, Ouki SK (2012). Solidification/stabilisation of electric arc furnace waste using low grade MgO. *Chemosphere*, 86(8): 789–796.

Cushnie GC (1994). *Pollution prevention and control technology for plating operations*. National Centre for Manufacturing Sciences, Ann Arbor, MI.

Da Silva CE, Benedetto JS, Tambourgi EB (1999). *Proceedings of International Solvent extraction Conference'99*. Barcelona, Pub. Society Chemical Industry, London: 189-194.

Dan Chena, Yang Li a, Jia Zhanga, Wenhui Li b, Jizhi Zhoua, Li Shaoa, Guangren Qiana, (2012). Efficient removal of dyes by a novel magnetic Fe₃O₄/ZnCr-layered double hydroxide adsorbent from heavy metal wastewater, *Journal of Hazardous Materials*, 243: 152-160.

Daniali S (1990). Solidification/Stabilization of heavy metals in latex modified portland cements matrices. *Journal of Hazardous Materials*, 24: 225-230.

Debroy M, Dara SS (1994). Immobilization of zinc and lead from wastes using simple and fiber-reinforced Lime pozzolana admixtures. *Journal of Environmental Science and Health*, 29: 339-355.

Demopoulos G.P., Li Z. Becze, L., Moldoveanu G., Cheng T.C., Harris B. (2008). New technologies for HCl regeneration in chloride hydrometallurgy. *World of Metallurgy: ERZMETALL*, 61(2): 89–98.

Desogus P., Manca P.P., Orrù G., Zucca A. (2013). Stabilization–solidification treatment of mine tailings using Portland cement, Potassium dihydrogen phosphate and ferric chloride hexahydrate, *Minerals Engineering*, 45: 47–54.

Di Luca CD (2011). Environmentally friendly system and method for manufacturing iron powder. US patent 20110300062.

Diaz G, Martin D, Frias C, Perez O (1999). Proceedings of International Solvent extraction Conference'99. Barcelona, Spain, Pub. Society Chemical Industry, London: 1449-1454.

Duche S N, Pawar SD, Dhadke PM (2002). Comparative study for extraction of Hg (II) with Cyanex-923 from chloride and bromide media and its separation from Cd (II) and Zn (II). *Separation Science and Technology*, 37: 2215-2229.

Eisa EH, Wafaa SH, Essam AK, Maha R M (2011). Solidification/stabilization of Ni (II) by various cement pastes. *Construction and Building Materials*, 25: 109–114.

El-Eswed B.I., Yousef R.I., Alshaaer M., Hamadne I., Al-Gharabli S.I., Khalili F. (2015). Stabilization/solidification of heavy metals in kaolin/zeolite based geopolymers, *International Journal of Mineral Processing*, 137: 34–42.

El-Nadi YA, El-Hefny NE (2010). Removal of iron from Cr-electroplating solution by extraction with di(2-ethylhexyl)phosphoric acid in kerosene. *Chemical Engineering and Processing*, 49: 159–164.

Espinosa DCR, Tenorio JAS (2000). Laboratory study of galvanic sludge's influence on the clinkerization process. *Resource, Conservation and Recycling*, 31: 71-82.

Eun Jung Kim, Eun-Ki Jeon, Kitae Baek (2016). Role of reducing agent in extraction of arsenic and heavy metals from soils by use of EDTA, *Chemosphere*, 152: 274–283.

Ferreira AS, Mansur M B (2011). Statistical analysis of the spray roasting operation for the production of high quality Fe_2O_3 from steel pickling liquors. *Process Safety and Environmental Protection*, 89: 172–178.

Forsell BA, Niklasson RJV (1974) Process for neutralization and regeneration of aqueous solution of acids and dissolved metals. US Patent 3800024.

Freshour AR, Thornton RF (2001). Acid recovery by diffusion dialysis, Environmental Laboratory, GE Corporate research and Development, Schenectady, NY.

http://ftp.jrc.es/pub/eippcb/doc/fmp_bref_1201.pdf [Available (Online)] Dated: 12/2/14

Fu YP (2006). Characterization of Ni–Cu–Zn Ferrite Prepared from Steel Pickling Liquor and Waste Solutions of Electroplating. *J. Am. Ceram. Soc.*, 89: 3547–3549.

Gálvez, J.L., Dufour, J., Negro, C., López-Mateos., F. (2006). Fluoride speciation in stainless steel pickling liquor. *The Iron and Steel Institute of Japan International*, 46(2): 281-286.

General Standards for Discharge of Environmental Pollutants (2009). Part-A: Effluents [Schedule – VI], *The Environment (Protection) Rules*: 545-548.

Geoffrey Michael Gadd (2009). Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. *J Chem Technol Biotechnol*, 84: 13–28.

Graaff JWM (1998). Acidic waste disposal by underground injection. *Journal of Geochemical Exploration*, 62: 325–329.

Gülay Bayramog̃lu, Yakup Arıca M. (2009). Construction a hybrid biosorbent using *Scenedesmus quadricauda* and *Ca-alginate* for biosorption of Cu (II), Zn (II) and Ni (II): Kinetics and equilibrium studies, *Bioresource Technology*, 100: 186–193.

Gupta B, Tandon SN, Deep A (2002). Proceedings of International Solvent extraction Conference'02. Cape Town: 793-795.

Gupta Vinod K, Nayak Arunima, Agarwal Shilpi (2015). Bioadsorbents for remediation of heavy metals: Current status and their future prospects, *Environ. Eng. Res.*, 20(1): 1-18.

Hamta Afshin, Dehghani Mohammad Reza (2017) Application of polyethylene glycol based aqueous two-phase systems for extraction of heavy metals, *Journal of Molecular Liquids*, 231: 20–24.

Heckley P, Ibana D (2000). Paper presented at new generation nickel laterites in the eastern goldfields, Australia. WMC Conf. Centre, Kalgoorlie.

Hills CD, Sollars CJ, Perry R (1993). Ordinary Portland Cement Based Solidification of Toxic Wastes, The Role of OPC Reviewed. *Cement and Concrete Research*, 23: 196-212.

Hoak DR, Lewis C J (1945). Treatment of spent pickling liquor with Limestone and Lime. *Industrial and Engineering Chemistry*, 37: 553-559.

Hoak DR, Lewis CJ (1947). Lime Treatment of Waste Pickling Liquor. *Industrial and Engineering Chemistry*, 39: 131-135.

Hoak DR, Lewis CJ (1948). Pickle liquor neutralization- economic and technology factor. *Industrial and Engineering Chemistry*, 40: 2062-2067.

Hoak DR, Lewis CJ (1949). New technology for waste pickling liquor neutralization. *Industrial and Engineering Chemistry*, 41(11): 65-70.

Hyun-Taek Kim, Tai Gyu Lee (2017). A simultaneous stabilization and solidification of the top five most toxic heavy metals (Hg, Pb, As, Cr, and Cd), *Chemosphere*, 178: 479–485.

Integrated Pollution Prevention and Control (IPPC), Reference document on best available techniques in the ferrous metals processing industry, December 2001.

Ito M, Tachibana R, Fukushima K, Seino Y, Yamamoto A, Kawabata Y (1998). Characteristics and Production: mechanism of sulfuric acid and nitric-hydrofluoric acid pickling sludge produced in manufacture of stainless steel. *Journal of Chemical Engineering of Japan*, 31: 589-595.

Ivey DG, Heimann RB, Neuwirth M, Shumborski S, Conrad D, Mikula RJ, Lam WW (1990). Electron microscopy of heavy metal waste in cement matrices. *Journal of Material Science*, 25: 5055-5062.

Janne Pesonen, Juho Yliniemi, Mirja Illikainen, Toivo Kuokkanen, Ulla Lassi (2016). Stabilization/solidification of fly ash from fluidized bed combustion of recovered fuel and biofuel using alkali activation and cement addition, *Journal of Environmental Chemical Engineering*, 4(2): 1759–1768.

Jha MK, Kumar V, Singh JR (2002). Solvent extraction of Zinc from Chloride Solutions. *Solvent extraction and Ion Exchange*, 20: 389–405.

Jha MK, Kumar V, Singh RJ (2001). Review of hydrometallurgical recovery of zinc from industrial wastes. *Resources, Conservation and Recycling*, 33: 1–22.

Jianli M, Youcai Z, Jinmei W, Li W (2010) Effect of magnesium oxychloride cement on stabilization/ solidification of sewage sludge. *Construction and Building Materials*, 24: 79–83.

Katsioti M, Katsiotis N, Rouni G, Bakirtzis D, Loizidou M (2008). The effect of bentonite/cement mortar for the stabilization/solidification of sewage sludge containing heavy metals. *Cement & Concrete Composites*, 30: 1013–1019.

Kindness A, Macias A, Glasser FP (1994). Immobilization of chromium in cement matrices. *Waste Management*, 14: 3-11.

Kittisupakorn P, Tangteerasunun P, Thitiyasook P (2005). Dynamic neural network modelling for hydrochloric acid recovery process. *Korean Journal of Chemical Engineering*, 22: 813-821.

Lawson KW, Lloyd DR (1997). Membrane distillation. *Journal of Membrane Science*, 124: 1–25.

Lee CH, Wang HC, Lin CM, Yang GCC (1994). A long-term leachability study of solidified wastes by the multiple toxicity characteristic leaching procedure. *Journal of Hazardous Materials*, 38: 65–74.

Li X. M., Zhao J. X., Cui Y. R., Yang J. (2009). The comprehensive utilization of eaf dust and pickling sludge of stainless steel works, *Materials Science Forum*, 620-622: 603-606.

Liu CW, Lin CH, Fu YP (2007). Characterization of Mn–Zn ferrite prepared by a hydrothermal process from used dry batteries and waste steel pickling liquor. *J. Am. Ceram. Soc.*, 90(10): 3349–3352.

Liu NW, Chou MS, Degree of hazardous reduction of secondary aluminium dross using ferrous chloride (2013). *J. Hazard. Toxic Radioact. Waste*, 17(2): 120-124.

Lopez F. A. , Gonzalez P. , Garcia F. J. , Rubio A. , Lopez-Delgado A. (1997). Iron oxidation of sulfuric water pickling liquors by *Thiobacillus Ferrooxidans* and crystallisation of ferric and ammonium sulphates, *Biotechnology for Waste Management and Site Restoration NATO ASI Series*, 34: 107-115.

Lum KH, Stevens G, Perera JM, Kentish SE (2013). The modelling of ZnCl₂ extraction and HCl co-extraction by TBP diluted in ShellSol 2046. *Hydrometallurgy*, 133: 64–74.

Lum KH, Stevens GW, Kentish SE (2012). The modelling of water and hydrochloric acid extraction by tri-n-butyl phosphate. *Chemical Engineering Science*, 84: 21–30.

Luo J, Wu C, Xu T, Wu Y (2011). Diffusion dialysis-concept, principle and applications. *Journal of Membrane Science*, 366: 1–16.

Macias A, Kindness A, Glasser FP (1997). Impact of carbon dioxide on the immobilization potential of cemented wastes: chromium. *Cement and Concrete Research*, 27: 215-225.

Macphee DE, Glasser FP (1993). Immobilization science of cement systems. *MRS Bulletin*, 3: 66-71.

Mantius Otto (1938). Improvements in and Relating to processes of recovering sulphuric acid from sulphuric acid. United Kingdom Patent GB483821.

Margaryan Armine (2012). New metal-tolerant *bacilli* strains as a prospective tool for bioremediation, 5th International Symposium on biosorption and Bioremediation, Prague, June 24-25: 22-28.

Marta Izquierdo, Carmen Gabaldón and Paula Marzal (2012). Influence of the presence of complexing agents on the copper (II) biosorption onto *posidonia oceanica* from metal plating wastewater, 5th International Symposium on Biosorption and Bioremediation, Prague, June 24-25: 18-21.

Marzieh Safari, Ali Sorooshzadeh, Ahmad Asgharzadeh and Saeed Saadat (2012). Modeling adsorption of cadmium by plant growth promoting rhizobacteria at different pH solution, 5th International Symposium on biosorption and Bioremediation, Prague, June 24-25: 38-42.

Minocha AK, Jain Neeraj, Verma CL (2003). Effect of inorganic materials on the solidification of heavy metal sludge. *Cement and Concrete Research*, 33: 1695-1701.

Mishra RK, Rout PC, Sarangi K, Nathsarma KC (2010). A comparative study on extraction of Fe (III) from chloride leach liquor using TBP, Cyanex 921 and Cyanex 923. *Hydrometallurgy*, 104: 298–30.

Montañés M.T., Sánchez-Tovar R., Roux M.S. (2014). The effectiveness of the stabilization/solidification process on the leachability and toxicity of the tannery sludge chromium, *Journal of Environmental Management*, 143(1): 71–79.

Mughal ST, Tahira S, Tayyaba A, Farzana B (2008). Treatment of electroplating effluent. *J. Chem. Soc. Pak.*, 30: 29-32.

Narasimhan BRV, Kumar Satendra, Narayanan TSN (2011). Synthesis of manganese zinc ferrite using ferrous pickle liquor and pyrolusite ore. *Environ Chem Lett*, 9: 243–250

Narvaez L, Cano E, Bastidas DM (2005). 3-Hydroxybenzoic acid as AISI 316L stainless steel corrosion inhibitor in a H_2SO_4 -HF- H_2O_2 pickling solution. *Journal of Applied Electrochemistry*, 35: 499–506.

Oh SJ, Moon SH, Davis T (2000). Effect of metal ions on diffusion dialysis of inorganic acids. *Journal of membrane science*, 169: 95-105.

Owens JW, Stewart S (1996). Cement binders for organic wastes. *Magazine of Concrete Research*, 48: 37-44.

- Ozdemir T, Oztin C, Kincal NS (2006). Treatment of waste pickling liquors: process synthesis and economic analysis. *Chem Eng Commun*, 193: 548–563.
- Palmer C. Mervin (1969). A composite rating of algae tolerating organic pollution. *Journal of Phycology*, 5(1): 78–82.
- Panigrahi S., Parhi P.K., Sarangi K., Nathsarma K.C. (2009). A study on extraction of copper using LIX 84-I and LIX 622N, *Separation and Purification Technology*, 70(1): 58–62.
- Peterson JC, Salof GA (1991). Process and apparatus for the low temperature recovery of ferrous chloride from spent hydrochloric acid. U S Patent 5057290.
- Raymond LA, Stephen LJ (2009). Acid recycle process with iron removal. US patent 20090145856.
- Reddy MLP, Saji J (2002). Proceedings of Chloride Metallurgy '02, 32nd Annual Hydrometallurgy Meeting. Montreal, CIM: 513-525.
- Regel- Rosocka M (2010). A review on methods of regeneration of spent pickling solution from steel processing. *J. Hazardous Material*, 177: 57-69.
- Regel-Rosocka M, Miesac I, Sastre AM, Szymanoski J (2002). Proceedings of International Solvent extraction Conference'02. Cape Town, South Africa: 768-773.
- Roberto Pérez-Garibay, Javier Martínez-Jiménez, Alejandro Uribe-Salas, Martínez-Luévanos (2012). Antonia Comparative Study between D2EHPA and Cyanex 272 as Extractants of Mn(II) from a Leached Liquor Produced by Reductive Leaching of a Pyrolusite Ore with SO₂, *Engineering*, 4: 526-53.
- Rosinda M, Ismael C, Carvalho R (2002). Proceedings of International Solvent extraction Conference'02. Cape Town, South Africa: 781-786.
- Roy A, Cartledge FK (1997). Fundamental aspects of cement solidification and stabilization. *Journal of Hazardous Materials*, 52: 151-354.

- Roy A, Eaton HC, Cartledge FK (1991). Solidification/Stabilization of heavy metal sludge by a portland cement/fly ash binding mixture. *Hazardous Waste and Hazardous Materials*, 8: 33-41.
- Roy A, Eaton HC, Cartledge FK, Tittlebaum ME (1992). Solidification/Stabilization of hazardous waste: evidence of physical encapsulation. *Environmental Science and Technology*, 26: 1349-1353.
- Roy A, Eaton HC., Cartledge FK, Tittlebaum ME (1993). Solidification/Stabilization of a synthetic electroplating sludge in cementitious binders containing NaOH. *Journal of Hazardous Materials*, 35: 53-71.
- Sahu SK, Verma K, Vijay BD, Kumar V, Pandey, B D (2008). Recovery of Cr (VI) from electroplating effluent by solvent extraction with tri-n- butyl phosphate. *Indian Journal of Chemical Technology*, 15: 397-402.
- Saji J, Rao TP, Iyer CSP, Reddy MLP (1998). Extraction of Iron III/ from acidic chloride solutions by Cyanex 923. *Hydrometallurgy*, 49: 289–296.
- Salman H. Abbas, Ibrahim M. Ismail, Tarek M. Mostafa, Abbas H. Sulaymon (2014). Biosorption of Heavy Metals: A Review. *Journal of Chemical Science and Technology*, 3(4): 74-102.
- Scholz W, Lucas M (2003) Techno-economic evaluation of membrane filtration for the recovery and re-use of tanning chemicals. *Water Research*, 37: 1859–1867.
- Shaikh L, Pandit A, Ranade V (2013). Crystallisation of ferrous sulphate heptahydrate: experiments and modelling. *The Canadian Journal of Chemical Engineering*, 91: 47 -54.
- Singhal A, Prakash S, Tewari VK (2007). Trials on sludge of lime treated spent liquor of pickling unit for use in the cement concrete and its leaching characteristics. *Building and Environment*, 42: 196-202.
- Singhal A, Prakash S, Tewari VK (2008a) Utilization of treated spent liquor sludge with fly ash in cement and concrete. *Building and Environment*, 43: 991-998.

Singhal A, Prakash S, Tewari VK (2008b) Characterization of stainless steel pickling bath sludge and its solidification/stabilization. *Building and Environment*, 43: 1010-1015.

Singhal Anupam, Prakash Satya, Tewari V.K. (2012) , A study on utilization of treated spent liquor sludge with fly ash by making cement concrete hollow cavity bricks, *International Journal of Environmental Protection*, 2 (9): 17-21.

Sisca O. Lesmana, Novie Febriana, Felycia E (2009). Soetaredjoa, Jaka Sunarsob, Suryadi Ismadjia. Studies on potential applications of biomass for the separation of heavy metals from water and wastewater, *Biochemical Engineering Journal*, 44: 19–41.

Stachera David M, Childs Ronald F, Mika Alicja M, Dickson James M (1998) Acid recovery using diffusion dialysis with poly(4-vinylpyridine)-Filled microporous membranes. *Journal of Membrane Science*, 148: 119-127.

Stevenson, EP (1924). Method of treating spent pickling liquor, U. S. Patent 1,515,799.

Stocks CP, Wood J, Guy S (2005). Minimization and recycling of spent acid wastes from galvanizing plants, *Resources. Conservation and Recycling*, 44: 153–166.

Sze YKP, Lam CSW, Long WK, Ho JMY (1999). Proceedings of International Solvent extraction Conference'99. Barcelona, Spain, Pub. Society Chemical Industry, London: 231-235.

Tamas FD, Csetenyi L, Tritthart E (1992). Effect of adsorbent on the leachability of cement bonded electroplating wastes. *Cement and Concrete Research*, 22: 399–404.

Tanaka B, Kobayashi M, Seki T (2002). Proceedings of International Solvent extraction Conference'02. Cape Town: 787-792.

Tang B, Su W, Wang J, Fu F, Yu G, Zhang J (2012). Minimizing the creation of spent pickling liquors in a pickling process with high-concentration hydrochloric acid solutions: Mechanism and evaluation method. *Journal of Environmental Management*, 98: 147-154.

Tang B, Yuan L, Shi T, Yu L, Zhu Y (2009). Preparation of nano-sized magnetic particles from spent pickling liquors by ultrasonic-assisted chemical co-precipitation. *Journal of Hazardous Materials*, 163: 1173–1178.

Temyanko V L (2003). Ferrous chloride conversion. US patent 2003021103.

The Gazette of India, Extraordinarily, Part-11, Section 3, Sub-section (ii), published by Authority No. 471, New Delhi, Wed, Feb 18, 2009, Min. Of Environment & Forest, Notification, New Delhi, 20th May, 2003.

Tomaszewska M, Gryta M, Morawski AW (1998). The influence of salt in solutions on hydrochloric acid recovery by membrane distillation. *Separation and Purification Technology*, 14: 183–188.

Vijay R, Sihorwala TA (2003). Identification and leaching characteristics of sludge generated from metal pickling and electroplating industries by toxicity characteristic leaching procedure (TCLP). *Environmental monitoring and assessment*, 84: 193-202.

Vijayaraghavan K., Yun Yeoung-Sang (2008). Bacterial biosorbents and biosorption, *Biotechnology Advances*, 26: 266–291.

Voglar GE, Lestan D (2011). Efficiency modelling of solidification/stabilization of multi-metal contaminated industrial soil using cement and additives. *Journal of Hazardous Materials*, 192: 753– 762.

Wagiwalla KM (2012). Synthesis of mass integration networks: Integrated approach to optimization of stream matching for a metal pickling process. *Computers and Chemical Engineering*, 44: 11– 19.

Wang K, Li J, McDonald RG, Browner RE (2011). The effect of iron precipitation upon nickel losses from synthetic atmospheric nickel laterite leach solutions: Statistical analysis and modelling. *Hydrometallurgy*, 109: 140–152.

Wang SY, Vipulanandan C (1996). Leachability of lead from solidified cement-fly ash binders. *Cement and Concrete Research*, 26: 895-905.

Weitzman L, Conner JR (1989). Descriptions of solidification/stabilization technologies, Immobilization technology seminar—speaker slide copies and supporting information, U.S. EPA, CERI: 89-222.

Weng CH, Huang CP (1994). Treatment of metal industrial wastewater by fly ash and cement fixation. *Journal of Environmental Engineering*, 120: 1470-1488.

Whetzel JC, Zimmerman RE (1935). Methods of recovering salts and other compounds. US Patent 2,005,120.

Winter DJ (2009). Processing of metal chloride solutions and method and apparatus for producing direct reduced iron. US Patent 20090095132.

Xiaojia Guo, Wenhui Yao, Yuehua Chen, Jing Fan, Yang Zhao, Jianji Wang (2017). PEG-functionalized ionic liquids: A class of liquid materials for highly efficient extraction of rare earth metals from aqueous solutions, *Journal of Molecular Liquids*, 236: 308–313.

Yang GCC (1993). Durability study of a solidified mercury-containing sludge. *Journal of Hazardous Materials*, 34: 217-223.

Yang GCC, Chang CF (1994a). Long-term stability of superplasticized monoliths of a solidified electroplating sludge. *Journal of Hazardous Material*, 37 (2): 277-283.

Yang GCC, KL Kao (1994b). Feasibility of using a mixture of an electroplating sludge and calcium carbonate sludge as a binder for sludge solidification. *Journal of Hazardous Materials*, 36: 81-88.

Zhang Huaiwei, Hong Xin (2011). An overview for the utilization of wastes from stainless steel industries *Resources, Conservation and Recycling*, 55(8): 745-754.

Zhou H, Smith DW (2002). Advanced technologies in water and wastewater treatment. *J. Environ. Eng. Sci*, 1: 247-264.

Zhuo Zhang, Guanlin Guo, Yanguo Teng, Jinsheng Wang, Jae Seong Rhee, Sen Wang, Fasheng Li (2015). Screening and assessment of solidification/stabilization amendments

suitable for soils of lead-acid battery contaminated site, *Journal of Hazardous Materials*, 288: 140–146.

Zorigtkhuu D, Kim YS, Kim H, Suh Y K (2006). Manufacture of an oil-based Fe-Co magnetic fluid by utilization of the pickling liquid of steel. *Metals and Materials International*, 12: 517-523.

Zu mriye Aksu, Ferda Go nen, Zafer Demircan (2002). Biosorption of chromium (VI) ions by Mowital B30H resin immobilized activated sludge in a packed bed: comparison with granular activated carbon, *Process Biochemistry*, 38: 175-186.

Chapter 3

Treatment of SPL

This chapter includes the treatment of SPL by conventional and biosorption method respectively.

3.1 Introduction

SPL is listed in hazardous waste according to EPA and hazardous waste management rule (MoEF, 2009). In normal practice, the SPL is treated with lime and lot of sludge is generated during the treatment process. This chapter includes the treatment of SPL by following ways:

- a) SPL treatment with different neutralizing agent to minimize the generation of sludge
- b) SPL treated with biosorption method with different biosorbent.

This chapter contains the detail of materials used in experiment, experimental techniques and the processes used for collection, characterization and testing of samples. Moreover, the results obtained during the treatment of SPL are discussed in detail. We have discussed about the sample collections, its preservation and treatment of SPL.

3.2 Sample Collection and Preservation

Samples were collected from steel industries; Industrial area of Haridwar (Sample A) and Industrial area of Bhiwani district, Haryana (Sample B). Due to some confidential reason, the industries names are not cited in the thesis. The samples were collected from the galvanizing plant. Galvanization is the process of applying a protective zinc coating to mild steel prevents rusting. Prior to the galvanization process, pre-treatment of steel has been done to remove rust, grease and other materials from the surface of the steel. In these industries, mild steel sheets were pickled with the diluted hydrochloric acid. The spent liquor samples were collected from the hydrochloric acid bath.

All the liquid samples collected in HDPE (High Density Polyethylene) containers. Composite sampling was carried out for the collection of the samples, and sampling was performed at an interval of 4 hours for a total sampling time of 24 hours.

All the samples were preserved as per the Standard Methods for the Examination of Water and Wastewater (Standard Methods, 1998).

3.3 Minimization of Sludge Generation

Spent baths must be disposed of because the efficiency of pickling decreases with increasing content of dissolved metals in the bath. The convenient and economical treatment method for waste pickling liquor in developing the country as India, where approximately 30 million's Micro, Small & Medium Enterprises (MSMEs) exist is precipitation/ neutralization, under appropriate pH conditions (Galvez, 2008)). MSME sector of India is considered as the backbone of the economy, contributing to 45% of the industrial output, 40% of India's exports and produce more than 8000 quality products for the Indian and international markets (http://www.eisbc.org/Definition_of_Indian_SMEs.aspx :- Dated 23rd April 2014). The drawback of this treatment process is that it generates a huge amount of sludge. Therefore, it requires vast land to dispose of the precipitate and it will increase the treatment cost. The sludge generated during the treatment process is disposed into the low-lying area without proper treatment. The leachate of sludge may contaminate the groundwater because it contains the heavy metals. To remove these drawbacks a study has been undertaken to minimize the generation of the pickling sludge by using different neutralizing agents and their combination.

Table 3.1: Different types of neutralizing agents (Barar, 2010)

S. No	Name	Molecular Formula	Molecular weight (g)	Max pH
1	Ammonia solution	NH ₄ OH	35	11.63
2	Calcium carbonate	CaCO ₃	100	9.4
3	Calcium oxide	CaO	56	12.45
4	Calcium hydroxide	Ca(OH) ₂	74	12.4
5	Magnesium carbonate	MgCO ₃	84	10.9
6	Magnesium hydroxide	Mg(OH) ₂	58	10.6
7	Potassium hydroxide	KOH	56	14
8	Sodium carbonate	Na ₂ CO ₃	106	11
9	Sodium hydroxide	NaOH	40	14

Treated effluent was analyzed as per standard methods (Standard methods, 1998). Different types of neutralizing agents are available (Table 3.1) in the market. Calcium hydroxide, Potassium hydroxide, and Sodium hydroxide were selected for the study on the basis of their pH.

3.3.1 Material and procedure

Pickling effluent was treated with various neutralizing agents viz. Lime (CaO), Sodium hydroxide (NaOH), Potassium hydroxide (KOH) and their several combinations. Lime purity = 80% as CaO, NaOH = 97%, KOH = 84% has been taken for the study. In the treatment of pickling effluent, first of all, pH was raised up to 12-14 by lime, NaOH, KOH and their combination. After that alum was used to decrease pH up to 7. Free settling was allowed. The procedure of the treatment process is depicted in Figure 3.1.

Various combinations used for optimization of treatment and their designations are given in Table 3.2. All the experiments were performed in triplicate and the mean values are reported in the result with maximum 5% deviation in all cases performed.

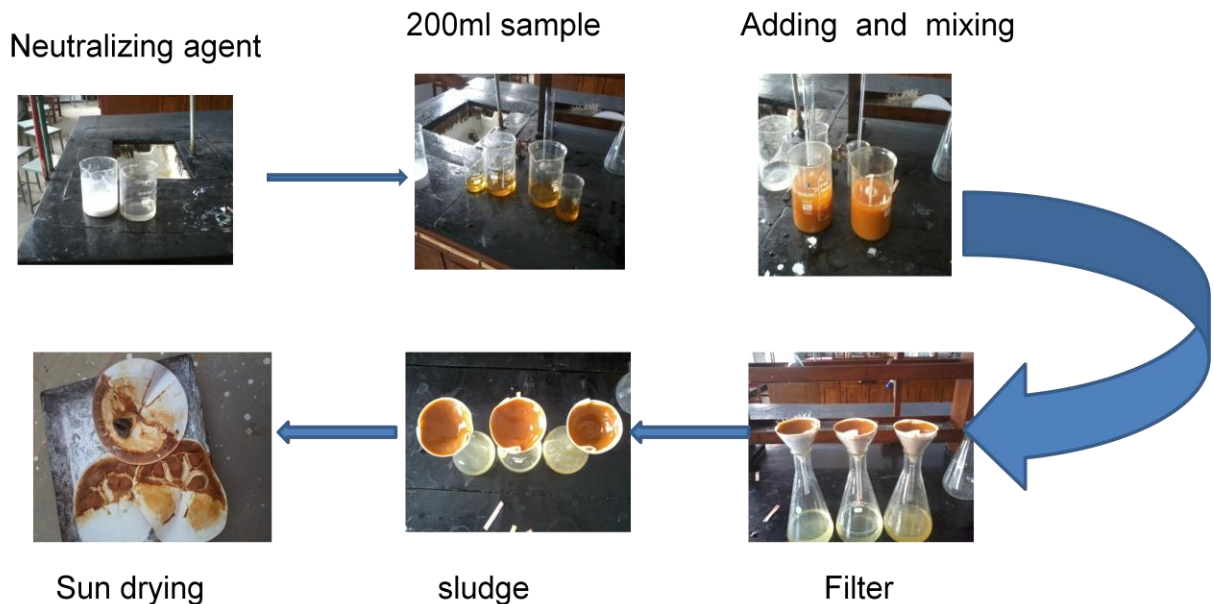


Figure 3.1: Sequence of steps involved in the treatment process

Table 3.2: Designation of samples with different combination for SPL treatment

Sample Code	Untreated pickling effluent volume (ml)	Calcium hydroxide (10% solution)*	Sodium hydroxide (10% solution)*	Potassium hydroxide (10% solution)*
N	200	-	100%	-
K	200	-	-	100%
LH	200	100%	-	-
KLH1	200	80%	-	20%
KLH2	200	60%	-	40%
KLH3	200	40%	-	60%
KLH4	200	20%	-	80%
NLH1	200	80%	20%	-
NLH2	200	60%	40%	-
NLH3	200	40%	60%	-
NLH4	200	20%	80%	-

Note- Weight/Volume (W/V)*

Notations: LH- Lime, K-Potassium, and N-Sodium

3.3.2 Characterization of spent liquor and treated liquor

Spent liquor was characterized by the following methods:

- a) pH and Total dissolved solids (TDS) were determined by Digital pH meter (sensION, MM150 meter, HACH, Barcelona, Spain; Figure 3.2) with a combined electrode as per Standard Methods for Examination of Water & Wastewater (Standard Methods, 1998).
- b) Dissolved oxygen (DO) was determined by digital DO pen (Model: AE 24878, Sper scientific, Taiwan; Figure 3.3) as per Standard Methods for Examination of Water & Wastewater (Standard Methods, 1998).



Figure 3.2: pH and TDS meter



Figure 3.3: DO meter

- c) COD was determined by Spectrophotometer: The samples for COD testing were prepared by adding 0.25 ml COD solution 1 (mercuric sulfate and sulfuric acid) and 2.80 ml COD solution 2 (silver sulfate, chromic acid, sulfuric acid and demineralize water) in a 2 ml sample and kept for digestion in Digital Reactor Block 200 (DRB 200) (Figure 3.4) for 2 hrs at 120 °C. After that, the samples were allowed to cool and COD was analyzed in Spectrophotometer DR2700, Hach, Germany (Figure 3.5).



Figure 3.4: COD Digester



Figure 3.5: Spectrophotometer DR2700

- d) Total Iron (Fe) was determined by Evolution 201 UV-Visible Spectrophotometers (Thermo Scientific, US; Figure 3.6).

Fe^{2+} present in the sample, quantitatively make complexed with 1,10-phenanthroline in the pH range from 3 to 9 to produce an intensely red-orange colored complex. Sodium acetate was used as a buffer to maintain a constant pH at 3.5. The determination of the iron-phen complex was performed with a spectrophotometer at a fixed wavelength of 508 nm using external calibration based on iron standard solutions.



Figure 3.6: Evolution 201 UV-Visible Spectrophotometers

UV spectroscopy obeys the Beer-Lambert law, which states that: when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with the thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution. The expression of Beer-Lambert law is by Equation 3.1

$$A = \log \left(\frac{I_0}{I} \right) = \epsilon * C * L \quad (3.1)$$

Where, A = absorbance (unitless), I_0 = intensity of light incident upon a sample cell (candela), I = intensity of the light leaving sample cell (candela), C = molar concentration of solute (mol/L), L = length of sample cell (cm), ϵ = molar absorptivity (L/mol/cm).

The specification of UV Spectrophotometer is given in Annexure B.

3.3.2.1 XRF study

The X-ray Fluorescent Spectroscopy (XRF) analysis was carried out at the Aditya Birla Science & Technology Centre Limited, Mumbai, India using WD-XRF (S8 Tiger-Bruker) in accordance with ISO 9516-1:2003.

XRF Principle: The specimen is excited with the primary X-radiation. In the process electrons from the inner electron, shells are knocked. Electrons from outer electron shells fill the resultant voids emitting a fluorescence radiation that is characteristic of its energy distribution for a particular material. This fluorescence radiation is evaluated by the detector. By counting the number of photons of each energy emitted from a sample, the elements present may be identified and quantitated.

3.3.2.2 XRD analysis

Pickling bath sludge was characterized by X-ray Diffraction (XRD) analysis Rigaku Miniflex II, Benchtop X-ray Diffractometer (Figure 3.7). Scan speed was 2°/minute and Cu target was used for analysis under working conditions of 40 kV and 25 mA by using Nickel filter. Some of the X-rays were diffracted by the crystal surfaces and can be represented in the form of the diffraction pattern. XRD analysis of the sludge carried out to identify the different phases of the sludge. Sludge was ground by mortar pestle and sieved (passing through 75 μ). The sludge was taken to Physics Department, BITS Pilani for XRD analysis. The X-rays were generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produced constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law Equation 3.2

$$n\lambda = 2d/\sin\theta \quad (3.2)$$

where, n is a positive integer (1, 2, 3 etc), λ is the wavelength of x-rays (m), and moving electrons, protons and neutrons, d is the spacing between the planes in the atomic lattice (m), and θ is the angle between the incident ray and the scattering planes.



Figure 3.7: Rigaku Miniflex II, Benchtop X-ray Diffractometer

3.3.2.3 Particle size analysis

Sieve analysis of the pickling bath sludge carried out for particle size testing. Samples of 500 g oven dried at of 105 °C for 24 hrs pickling sludge was taken for analysis. The sieves were stacked with the coarsest at the top and the finest at the bottom. Sieving was carried out for 15 minutes. Oversize sludge particles were weighed to determine the percentage of retained particles. (Yarnton, 1962).

3.3.2.4 pH Value

Samples of 100 g sludge were mixed with 100 ml of distilled water in a beaker (1:1 ratio). Beaker was shaken well and allowed to dissolve the sludge in water for 10 minutes. The pH measured by dipping the electrode into the water.

3.3.2.5 Bulk density

Oven dried sludge was filled in a cylinder of known dimensions. The following Equation 3.3 measured bulk density.

$$\text{Bulk density} = \frac{\text{weight of the sludge (kg)}}{\text{Volume of the cylinder (m}^3\text{)}} \quad (3.3)$$

3.3.2.6 Moisture content of the sludge

Samples of 1g sludge were taken in a porcelain crucible. It was kept in an oven at a temperature of 105 ± 2 °C for 2 hours. Crucible was cooled in a desiccator. Moisture content was calculated using Equation 3.4.

$$\text{Moisture (\%)} = \frac{\text{Initial weight of sludge} - \text{Dried weight of sludge}}{\text{Initial weight of sludge}} * 100 \quad (3.4)$$

3.3.2.7 Loss on ignition

Samples of 1 g of oven dried sludge were taken in a platinum crucible. These were kept in a muffle furnace at a temperature of 1050 °C for 1 hour. Crucible was cooled in a desiccator. Loss of ignition was computed using Equation 3.5.

$$\text{Loss of Ignition (\%)} = \frac{\text{Initial weight of sludge} - \text{Final weight of sludge}}{\text{Initial weight of sludge}} * 100 \quad (3.5)$$

3.4 Results and Discussions

3.4.1 Characteristics of spent pickling liquor sample

SPL sample was procured from the Industrial area of Haridwar (Sample A). The study of sludge minimization SPL during its treatment was done by using Sample A. However, the biosorption study was performed on the Sample B (Industrial area of Bhiwani district, Haryana) due to non-availability of Sample A. The characterization of spent liquor from steel pickling industry is presented in Table 3.3. This is clear from the table that SPL is highly acidic ($\text{pH} < 2$), so it is corrosive in nature (Wentz, 1995).

Table 3.3: Characterization of pickling effluent

S. No.	Parameter	Sample from two industries	
		Sample A	Sample B
1	pH	0.37	0.94
2	Electrical Conductivity (EC) mS/cm	20	11
3	Temperature, °C	32	31
4	Total Dissolved Solids (TDS) g/l	13	8
5	Chemical Oxygen Demand (COD) mg/l	785	53
6	Iron g/l	5.65	5.1
7	Chloride mg/l	80	76

3.4.2 Result of treated SPL

The values of physical and chemical properties of treated effluent were found within the acceptable limits, after treatment with lime, NaOH, KOH and their combination. The color of treated sludge was fuller's earth color when SPL was treated with 100% lime only and brick red color when SPL was treated with 100% NaOH and 100% KOH as shown in Figure 3.8. The pH and dissolved oxygen (DO) value of treated SPL lie in the range of 7.0 to 7.8 and 2 to 4.3 mg/l respectively as given in Table 3.4. Graph of Conductivity and Total Dissolved Solids (TDS) are shown in Figure 3.9 and which confirms linear relationship between them.

The calculation of percentage reduction in TDS was done with respect to the untreated SPL. Treatment with a neutralizing agent and their combination reduces TDS by 62-78%. Percentage reduction of TDS is given in Figure 3.10. Highest reduction of TDS has been observed in the treatment of lime only (78%) and lowest (62.31%) in KLH4 (80% KOH + 20% lime). 100% NaOH and 100% KOH reduced TDS around 75% and 68% in the treated effluent respectively. The iron content in treated SPL was within the acceptable limit in all the cases.

Table 3.4: Treated SPL parameters

Sample Code	pH	EC (mS/cm)	TDS (g/l)	DO (mg/l)	Fe (mg/l)
N	7.7	5.1	3.3	4.3	2.12
K	7.5	6.5	4.2	4.2	2.83
LH	7.5	4.5	2.9	4	1.75
KLH1	7.12	6.00	3.9	2.5	2.56
KLH2	7.16	6.31	4.1	4.1	2.83
KLH3	7.18	6.46	4.2	2.2	2.86
KLH4	7.72	7.54	4.9	3	2.91
NLH1	7.07	4.92	3.2	2.4	2.05
NLH2	7.00	5.08	3.3	2.1	2.17
NLH3	7.12	6.00	3.9	2	2.52
NLH4	7.25	6.1	4.0	2.7	2.94



Calcium hydroxide sludge



Sodium hydroxide sludge



Potassium hydroxide sludge

Figure 3.8: Colors of treated sludge

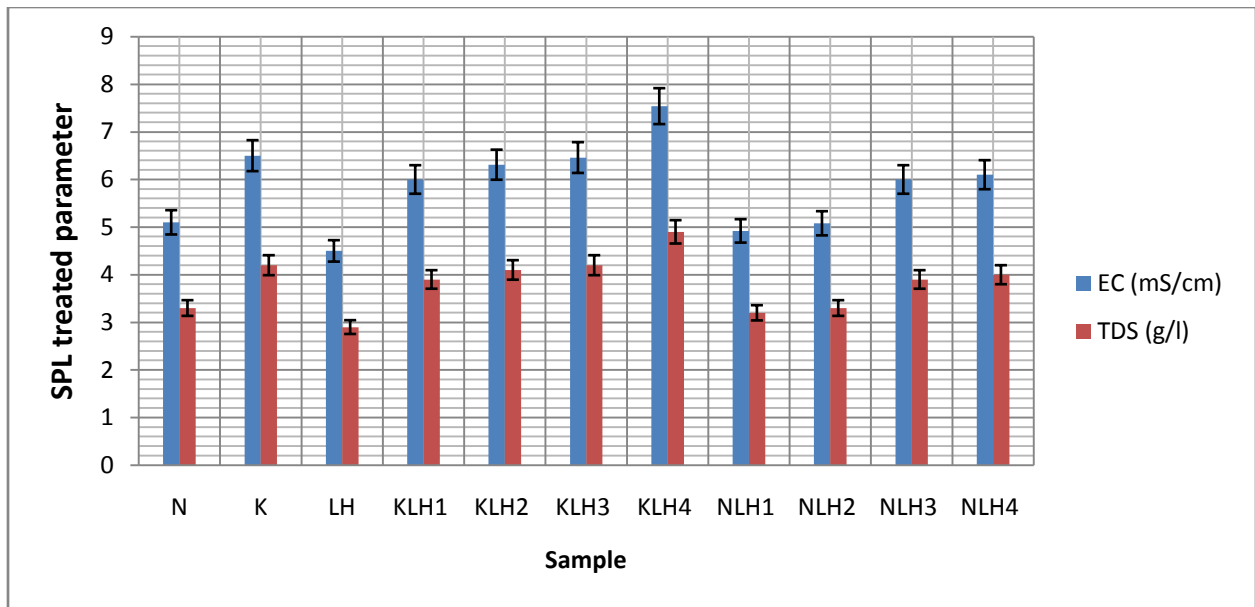


Figure 3.9: EC & TDS values of SPL treated samples

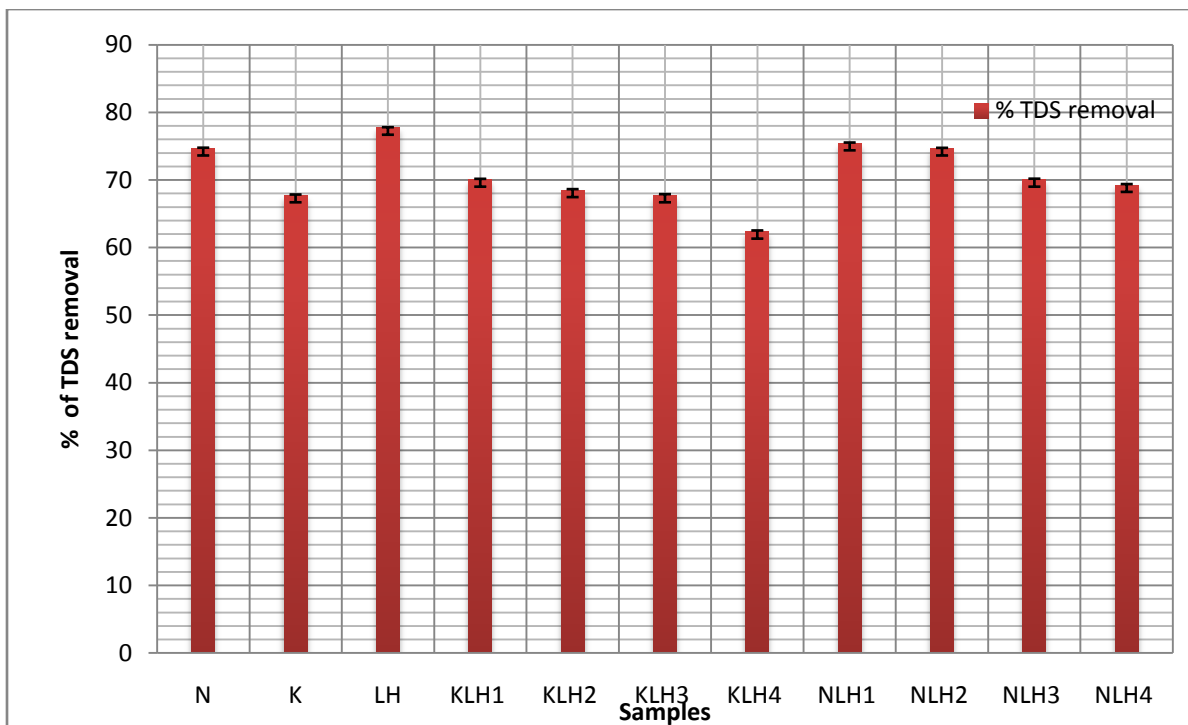


Figure 3.10: Percentage removal of total dissolved solids

3.4.3 Sludge generation

Sludge generation quantity after treatment of SPL by various neutralizing agents and their combination results are given in Table 3.5 Sample LH, which is 100% lime, taken as a base for comparison of sludge generation and treatment cost. It is evident from Table 3.5 that the minimum sludge quantity was generated when SPL was treated with 100% KOH and maximum with 100% lime respectively. A 30% reduction of sludge generation quantity was observed in comparison to lime only when SPL treated with NaOH only. 100% KOH reduced around 59.5% sludge generation quantity in comparison to 100% lime. Sludge reduction percentage increased from 11 to 56% with a corresponding increase of KOH volume in the combination of lime and KOH. In a combination with lime and NaOH, sludge reduction increased from 25 to 34% with a corresponding increase of NaOH volume. The dosage of alkali and its pH plays an important role in the generation of sludge (Banu et al., 2012).

Table 3.5: Sludge generated during SPL treatment

Sample Code	Sludge generation in treatment of pickling effluent (quantity 200ml) (g)	% Reduction in sludge generation
N	14.11	28.70136433
K	8.13	58.91864578
LH	19.79	Control(sample LH taken as reference)
KLH1	17.83	9.903991915
KLH2	13.68	30.87417888
KLH3	13.98	29.35826175
KLH4	8.85	55.28044467
NLH1	13.94	29.56038403
NLH2	13.35	32.54168772
NLH3	11.6	41.38453765
NLH4	11.44	42.19302678

3.4.4 Economic analysis

In this section, the cost of treatment of SPL with lime, NaOH, KOH and their combination is discussed. The chemicals used in the treatment of SPL are given below with prices:

Cost of KOH pellets = Rs. 620 /kg

Cost of NaOH pellets = Rs. 228 /kg

Cost of Alum = Rs. 25 /g

Cost of Lime = Rs. 9 /kg

The cost of KOH pellets and NaOH pellets is more than 69 and 25 times of the cost of lime respectively. Table 3.6 shows the cost of treatment of SPL with lime, NaOH, KOH and their combinations. Although minimum sludge was produced by 100% KOH, its cost of treatment is almost 63 times more than that of lime and 16 times more than that of NaOH. It can be concluded from Figure 3.11 and Table 3.6 that NLH4 (20% lime and 80% NaOH) reduced sludge generation quantity by 34% and it is a viable economic solution for treatment of SPL without affecting the quality of treated SPL.

Table 3.6: Cost of various treatments

Sample Code	Calcium hydroxide used (ml)	Sodium hydroxide used (ml)	Potassium hydroxide used (ml)	Alum used (ml)	Cost of solution required for treatment of 200 ml sample (in Rs.)
N	-	350	-	20	7.99
K	-	-	550	50	34.11
LH	600	-	-	5	0.54
KLH1	400	-	90	30	6.02
KLH2	270	-	220	35	13.97
KLH3	225	-	290	40	18.28
KLH4	135	-	390	49	24.42
NLH1	320	65	-	20	1.82
NLH2	280	120	-	23	3.05
NLH3	210	200	-	25	4.81
NLH4	90	260	-	28	6.08

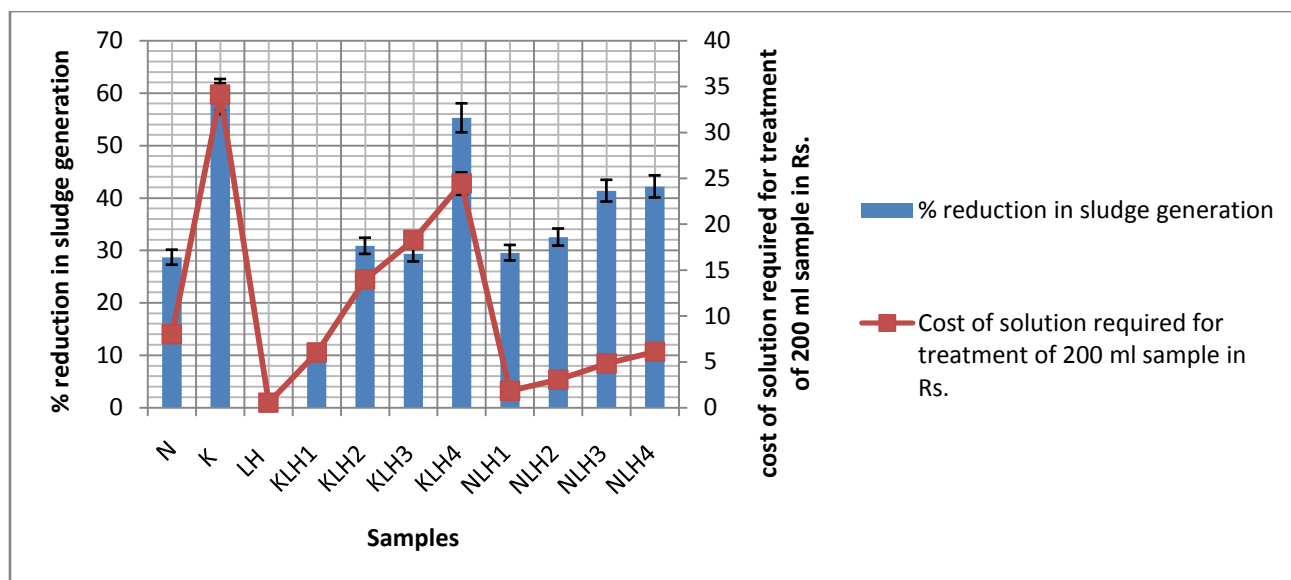


Figure 3.11: Percentage reduction in sludge generation and cost of solution required for treatment of 200 ml SPL samples.

3.4.5 Characterization of treated sludge

Three different types of neutralizing agents were used for the treatment of SPL. The sludge generated in the treatment process was characterized by XRD and XRF methods. Figure 3.12 shows the XRD pattern of the sludge of sample N. The XRD spectrum of sample N show the peaks at 32° , 45.5° , 56.5° and 66° , which confirm that it is a Sodium chloride (NaCl) compound. From the Figure 3.13, it can be observed that the sample K sludge is Potassium chloride as peaks are found at 28.5° , 40.6° , 50° , 59° , 66° (JCPDS, 1972). Sample KH sludge (Calcium Chloride) shows (Figure 3.14) the peaks at 23, 29.6, 31.2, 47.7, and 48.7 (JCPDS, 1972). XRD results in details of samples N, K and LH are given in Table 3.7.

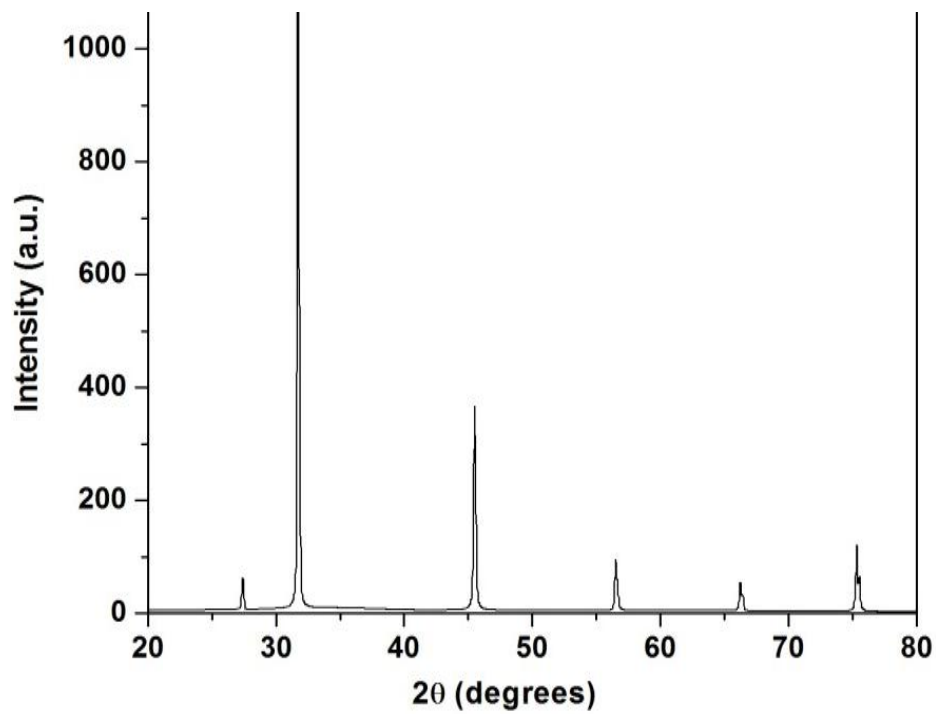


Figure 3.12: XRD spectrum of Sample N

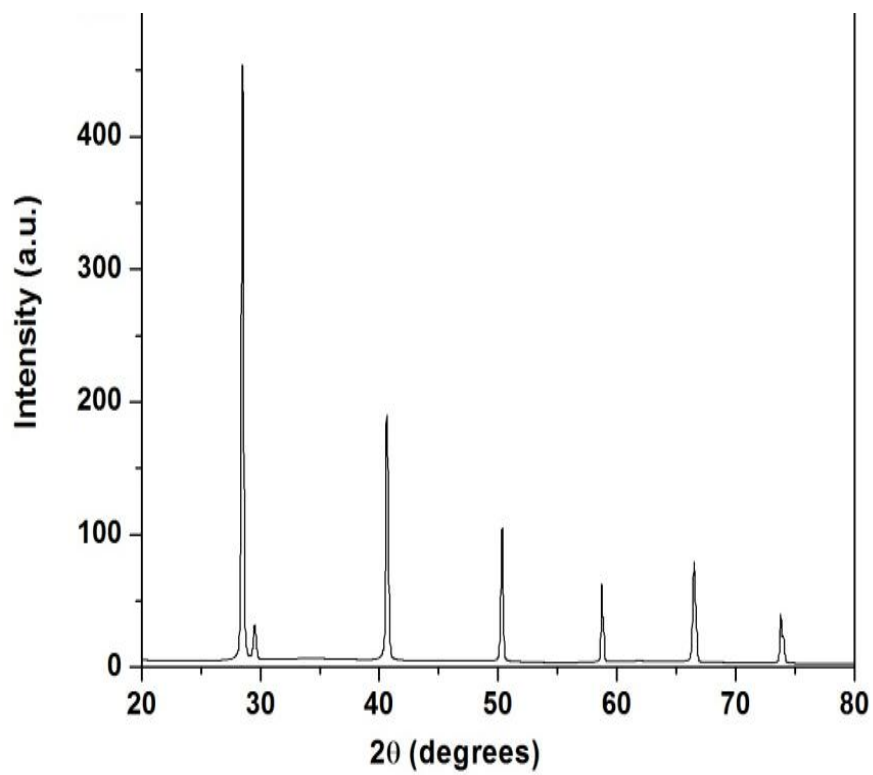


Figure 3.13: XRD spectrum of Sample K

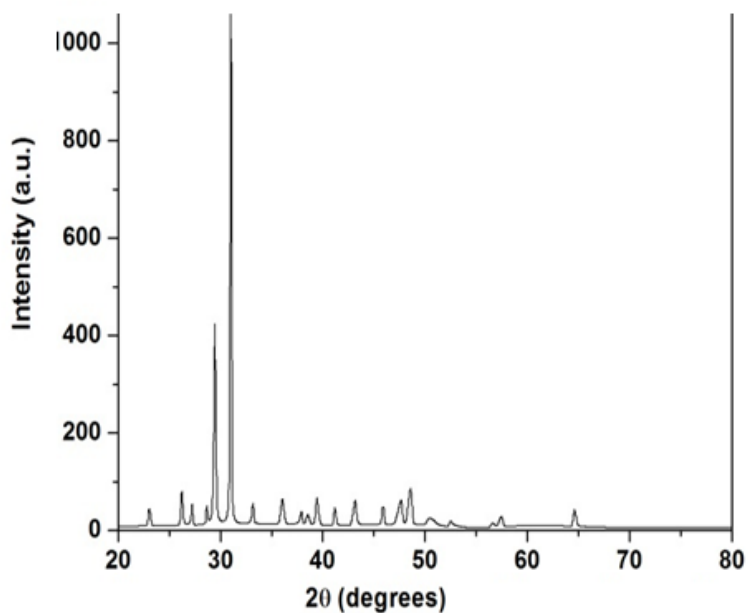


Figure 3.14: XRD spectrum of Sample LH

Table 3.7: Sludge Characterization by XRD

Sample	2 Theta (2θ)	d(Å)	Compound Identify
Sample N	32°	2.8	NaCl
	56.5°	1.63	
	45.5°	1.99	Fe
	66°	1.4	Fe ₂ O ₃
Sample K	28.5	3.12	KCl
	50°	1.81	
	59°	1.57	
	66°	1.4	Fe ₂ O ₃
Sample LH	23°	3.8	CaCl ₂
	29.6°	3.01	
	31.2°	2.86	Fe ₂ O ₃

Table 3.8: Sludge characterization by XRF

Sample	CaO%	O%	Cl%	MgO%	Fe ₂ O ₃ %	SiO ₂ %	Al ₂ O ₃ %	Na ₂ O%	K ₂ O%
Sample	-	23.21	17.13	0.26	6.67	0.41	9.94	42.42	-
Sample	-	26	13.31	0.13	6.34	0.11	8.85	-	55
Sample	71.52	26.32	12.45	6.19	6.12	1.87	0.4	-	-
KLH1	62.07	26.71	5.56	7.81	13.75	2.45	5.67		1.05
KLH2	58.48	26.31	6.81	6.65	13.56	2.34	6.86	-	2.65
KLH3	36.97	26.41	20.91	6.17	11.11	2.14	8.72	-	7.55
KLH4	19.02	26.07	17.94	3.67	18.5	1.95	14.62	-	19.77
NLH1	49.51	28.38	12.64	10.39	16.11	3.84	4.87	16.6	-
NLH2	45.16	27.92	12.85	8.89	16.28	3.3	4.85	17.7	-
NLH3	37.3	27.47	13.03	4.12	14.45	1.35	4.93	22.8	-
NLH4	32.18	27.41	13.12	3.13	14.7	1.08	5.03	31.57	-

Sludge characterizations of all samples were done by using the XRF method and results are incorporated in Table 3.8. The consumption of Calcium hydroxide was higher than Potassium, Sodium hydroxide, as the percentage of Calcium oxide in sludge is 71.52%, Potassium oxide 55%, and Sodium hydroxide is 43% when waste pickling liquor treated with 100% lime, Potassium hydroxide and Sodium hydroxide. Presence of magnesium and silica in sludge due to the presence of impurities in mild steel and a neutralizing agent. It can be observed from the results that the sludge generated in the treatment process is highly alkaline and contains macronutrients (viz. Calcium (Ca), Magnesium (Mg), Potassium (K) and Chloride (Cl⁻)) which are required for plants.

(<http://www.ncagr.gov/cyber/kidswrld/plant/nutrient.htm>: Dated: - 12th Nov 2013).

Therefore, some amount of sludge can be used as a fertilizer for plantation where soil has high acidity (Gazey and Davies, 2009).

3.5 Discussions

The economic treatment method of SPL for the MSMEs is neutralization method. Generally, Calcium hydroxide is used for the treatment of SPL due to its low price and easily available in the market, but it produces a lot of sludge and leads to disposal problem. Several neutralizing agents are present in the market. The dosage of alkali and its pH plays an important role in the generation of sludge (Banu et al., 2012). Therefore, Potassium hydroxide, Sodium hydroxide, and Calcium hydroxide were selected for the study based on their pH. Three different neutralizing agents viz. Potassium hydroxide, Sodium hydroxide and Calcium hydroxide and their combinations were used for the study of the sludge generation quantity in waste pickling liquor treatment. All the experiments were performed thrice with maximum 5% standard deviation in all cases performed. 100% Potassium hydroxide generated the lowest sludge, but the cost of Potassium hydroxide pellets is much higher than the Sodium hydroxide (the cost of Potassium hydroxide pellets is approx. 3 times of Sodium hydroxide pellets and 75 times of Lime). The cost and sludge generation of Sodium hydroxide is in between the Potassium and Lime. Therefore, the economic solution is to use 20% calcium hydroxide and 80% Sodium hydroxide for SPL treatment without much affecting the quality of treatment. Lower sludge generation will result in lower cost of sludge handling, i.e. sludge collection, transportation, and disposal arrangement.

Sludge characterization was done by XRD and XRF. The results revealed that the sludge generated in the treatment process is highly alkaline and contains macronutrients (viz. Calcium (Ca), Magnesium (Mg), Potassium (K) and Chloride (Cl⁻)) which are required for plants. Some amount of sludge can be used as fertilizer in plantations where soil has high acidity (Acid soil region in India is given in Annexure C) because the percentage of lime in the sludge is more than 71%. Industrial waste from paper mill, blast furnace, belit slag and ash from combustible deposits are already used as liming materials in agriculture for reclamation of acidic soil (Boris, 2009).

In next section, an attempt has been made to treat SPL by an environmentally friendly (biosorption) method. As biosorption have following advantages over chemical methods: biosorption is accomplished at a lower cost than conventional treatment methods; it has a higher efficiency, and the amount of sludge produced is reduced in biosorption process.

3.6 Biosorption of Spent Pickling Liquor

Various adsorbents were used for the treatment of spent pickling liquor. Mainly, low-cost adsorbents, such as agricultural wastes and microalgae were studied extensively due to their local availability. The lists of these agricultural wastes are listed in Table 3.9. These agricultural wastes were prepared for the experimentation by following steps (Marín et al., 2010):

- a) Materials rinsed with tap water several times and then with distilled water thrice to remove dirt and other particulate matter that might interact with sorbed metal ions.
- b) They were then air-dried at 50–60 °C until constant weight.
- c) The washed and dried material was crushed and sieved to obtain a particle size lower than 1.5 mm.

Table 3.9: List of materials used in the study

S. No.	Material Name	Scientific Name	Material Code	Form of material
1	Wheat Husk	<i>Triticum</i>	WH	Powder
2	Rice Husk	<i>Oryza sativa</i>	RH	Powder
3	Banana peel Husk	<i>Musa</i>	BH	Powder
4	Saw Dust	-	SD	Powder
5	Microalgae	<i>Scenedesmus</i> Sp.	SS	Powder

3.6.1 Microalgae cultivation

Microalgae *Scenedesmus* Sp. was procured from the Department of Biological Science, BITS Pilani, Pilani (Rajasthan) India, which was isolated from soil samples collected from textile and dyeing industrial site of Sanganer town situated at 26°49'N - 26°59'N and 75°46'E - 75°50'E near Jaipur district of Rajasthan, India (Sarwa and Verma, 2014). The microalgae were isolated using standard microbiological techniques and axenic cultures were maintained in a BG-11 medium under cool-white fluorescent, 1000 lux at 25 °C. The BG-11 medium composition is given Table 3.10 (Rippka et al., 1971).

Table 3.10: BG-11 medium composition

S. No.	Components	Concentration (g/l)
1	Sodium Nitrate	1.5
2	DiPotassium H Phosphate	0.04
3	MgSO ₄	0.075
4	CaCl ₂	0.036
5	Citric Acid	0.006
6	Ferric NH ₄ Citrate	0.006
7	EDTA	0.001
8	Na ₂ CO ₃	0.002
9	Trace Metal Mix	1 ml
Trace Metal Mix		
S. No.	Components	Concentration (g/l)
1	Boric Acid	2.86
2	MgCl ₂	1.81
3	ZnSO ₄	0.222
4	Sodium Molybdate	0.039
5	CuSO ₄	0.079
6	Cobalt Nitrate	0.0494

The *Scenedesmus* Sp. was cultured in the greenhouse of Department of Biological Science, BITS Pilani, Pilani (Rajasthan) India and the procedure is given below:

- a) The BG-11 medium chemicals were taken in a beaker and pour distill water to make a 1L solution.
- b) The solution was kept in stirring for 2 hrs for completely dissolving the chemical.
- c) 2 ml of algae solution was added to the beaker for the culture of algae.
- d) The culture was daily stirred to make the uniform composition of feed solution. Afterward, the cultured microalgae were filter and centrifuge.

3.6.2 Batch study

Initially, the experiments were performed by using SPL Sample B (Table 3.3). Afterward the experiments were performed by using artificial sample due to complexity in procuring the SPL sample from the industries. The artificial solution of SPL was prepared by dissolving 500 mg of pure Fe in 10% concentration of HCl in 1 liter as a stock solution and diluted for the experiments. The experiments were performed to determine the effect of various parameters (adsorbent dose, initial metal concentration, contact time and pH) on the sorption of Fe^{2+} onto Agriculture waste and algae. The mixture was stirred magnetically and the pH was continuously adjusted to the desired value, for all the assays, using small volumes of HNO_3 or NH_4OH dilute solutions. After 3 hrs, which is more than sufficient to reach equilibrium, samples were filtered through glass fiber prefilters (Millipore AP40) and the filtrates were analyzed for residual metal ion concentration by UV-Vis spectrophotometer (Thermo scientific Evolution 2001) at a 510 nm wavelength. Under the batch study, parameters were optimized:

- a) Contact Time
- b) Weight of Adsorbent
- c) Concentration of adsorbate
- d) pH

3.6.2.1. *Effect of adsorbent concentration*

The effect of adsorbent concentration on sorption of Fe (II) was obtained by adding 0.125 g, 0.25 g, 0.5 g, 0.75 g, 1 g, 1.5 g and 2.0 g of biosorbent to glass flasks containing SPL solution of 50 ppm of metal concentration with agitation at 200 rpm in an orbital shaker.

3.6.2.2. *Effect of contact time*

The experiments for determining the kinetics of the process were performed using 50 ppm from the initial metal concentration of Fe (II) ions. A 10 ml sample was collected at intervals of 10 minutes from (0–180 min) and was subsequently centrifuged at 1000 rpm for 5 minutes. Then the Fe (II) concentrations in the remaining solutions were measured by and the filtrates were analyzed for residual metal ion concentration by UV-Vis spectrophotometer.

3.6.2.3. Effect of initial concentration

The biosorption experiments were carried out using 1 g of biomass with concentrations of Fe (II) starting from 50 to 500 ppm of the solution. Shaking was affected at 200 rpm in an orbital shaker until equilibrium attained. Experiments were conducted at room temperature (25-28 °C). Then the biomass was removed and the iron concentration in the remaining solutions was measured by UV-Vis spectrophotometer. The amount of iron adsorbed by biomass was calculated using the Equation 3.6 (PerezMarín et al., 2010).

$$q_e = \frac{(C_i - C_e)}{M} V \quad (3.6)$$

Where, q_e is the specific metal biosorption (mg metal/g biomass), V is the volume of metal solution (l), C_i and C_e are the initial and equilibrium concentration of metal (mg metal/l), respectively, and M is the dry weight of the biomass (g).

3.6.2.4. Infrared analysis

A raw sample and biomass loaded with Fe (II) were analyzed using an infrared spectrophotometer (IR) Model 470 Shimadzu corporation adopting KBr disk technique, which was performed to give a qualitative and preliminary characterization of the main chemical groups present on the cell wall that is responsible for heavy metal biosorption. The FTIR specification is given in Annexure D. FTIR relies on the fact that the most molecules absorb light in the infrared region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule. The frequency ranges are measured as wave numbers typically over the range 4000 – 600 cm^{-1} .

3.6.2.5 Isotherms

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH. Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for

sufficient time, with its adsorbate concentration in the bulk solution in a dynamic balance with the interface concentration. Its physicochemical parameters together with the underlying thermodynamic assumptions provide an insight into the adsorption mechanism, surface properties as well as the degree of affinity of the adsorbents. There are many isotherms available to identify the adsorption mechanism and here we are using following two isotherms due to their universal acceptance.

Freundlich isotherm (Reynolds and Richard, 2009) is the mathematical relationship that describes the non-ideal and reversible adsorption and it is not restricted to the formation of a monolayer. This empirical model can be applied to multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. The amount adsorbed is the summation of adsorption on all active sites (each having bond energy). In multilayer adsorption, the stronger binding sites are occupied first, until adsorption energy is exponentially decreased upon the completion of adsorption process (Aravantinou et al., 2013). Graph between X and C_e is developed for Freundlich isotherm. The standard form of the isotherm is expressed by Equation 3.7 and its linear form by Equation 3.8.

$$q_e = X = K C_e^{1/n} \quad (3.7)$$

$$\log X = \log K + \frac{1}{n} \log C_e \quad (3.8)$$

Where, X = mass ratio of the solid phase- that is, the mass of adsorbed solute per mass of adsorbent, C_e = equilibrium concentration of solute, mass/volume (mg/l), K and n = Freundlich experiment constants (Reynolds and Richard, 2009).

Langmuir empirical model (Langmuir, 1918) assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. Homogeneous adsorption is referred in Langmuir isotherm which suggests that each molecule possesses constant enthalpies and sorption activation energy (all sites possess an equal affinity for the adsorbate) and no transmigration of the adsorbate in the plane of the surface occurs

(Aravantinou 2013). Graph between $1/X$ and $\frac{1}{C_e}$ is developed for plotting Langmuir isotherm. The standard form of the isotherm is expressed by Equation 3.9 and its linear form by Equation 3.10.

$$q_e = \frac{q_{\max} K C_e}{1 + K C_e} \quad (3.9)$$

$$\frac{1}{q_e} = \frac{1}{K q_{\max} C_e} + 1/Q_{\max} \quad (3.10)$$

Where, K = experiment constant or relative energy of adsorption (l/mg), C_e = equilibrium concentration of solute, mass/volume (mg/l), q_e = mass ratio of the solid phase, i.e., the mass of adsorbed solute per mass of adsorbent and Q_{\max} = ultimate adsorption capacity (mg/g)

3.6.2.6. Kinetics

Kinetic study Pseudo first-order and second-order kinetic models are used to explain the mechanism of the adsorption processes.

Pseudo-first order rate law, K_1

The formula for pseudo-first order kinetics is generally employed in the form proposed (Simonin, 2016) as Equation 3.11

$$\ln[q_e - q(t)] = \ln q_e - k_1 t \quad (3.11)$$

with q the amount of adsorbed solute, q_e its value at equilibrium, k_1 the pseudo-first order rate constant and t the time.

The integrated rate law after application of the initial condition of $q=0$ at $t=0$ may also be written in the following way, Equation 3.12

$$q(t) = q_e [1 - \exp(-k_1 t)] \quad (3.12)$$

A linear plot between $\log (q_e - q)$ and t was used for computation of the biosorption rate constant k_1 .

Pseudo-second order rate law, K_2

The formula for pseudo-second-order kinetics in the form proposed (Simonin, 2016) as Equation 3.13

$$\frac{t}{q(t)} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (3.13)$$

in which k_2 is the pseudo-second-order kinetic rate constant.

The integrated rate law after application of the initial condition of $q=0$ at $t=0$ may also be written in the following way, Equation 3.14

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t \quad (3.14)$$

A linear plot between t/q vs. t was used for computation of the biosorption rate constant k_2 .

3.6.2.7. Continuous study

The continuous biosorption experiments were carried out in an acrylic tubular column. The parameters of column study are noted in Table 3.11. The SPL solution was pumped upwards by a peristaltic pump at pH 6 and flow rate 8.5 ml/min to the column reactor. The specification of the peristaltic pump is given in Annexure E. The flow diagram of continuous study is depicted in Figure 3.15. The SPL solution was fed from the bottom of the reactor and effluent samples were collected at the top of the column during the time-course of the experiments. The treated effluent samples were collected at a regular time interval and analyzed using UV Spectroscopy. Each experiment was conducted continuously until the effluent Fe (II) concentration (C) approached the influent concentration (C_0), $C / C_0 = 0.99$.

The performance of the column bed is usually described through the concept of breakthrough curve, which is obtained by plotting the measured concentration divided by the inlet concentration (C/C_0) against time (t). Breakthrough and saturation time and Fe (II) uptake are relevant parameters that they can be obtained through the breakthrough curve.

Breakthrough time (t_b , min) is considered based on the effluent discharge limit for Fe (II). Consequently, the breakthrough time is used up at the point where the effluent solution Fe (II) concentration reaches to 3 mg/l (allowed limit in industrial effluent discharge).

Table 3.11: Parameters of column study

Parameter	Value
Height of column	32.5 cm.
Height of packed material in	18 cm.
Diameter of column	3 cm.
Mass of Material used in	24 g.
Flow Rate	8 ml/min (PerezMarín et al., 2010)
Initial Fe (II) concentration	20 mg/l , 50 mg/l and 100 mg/l

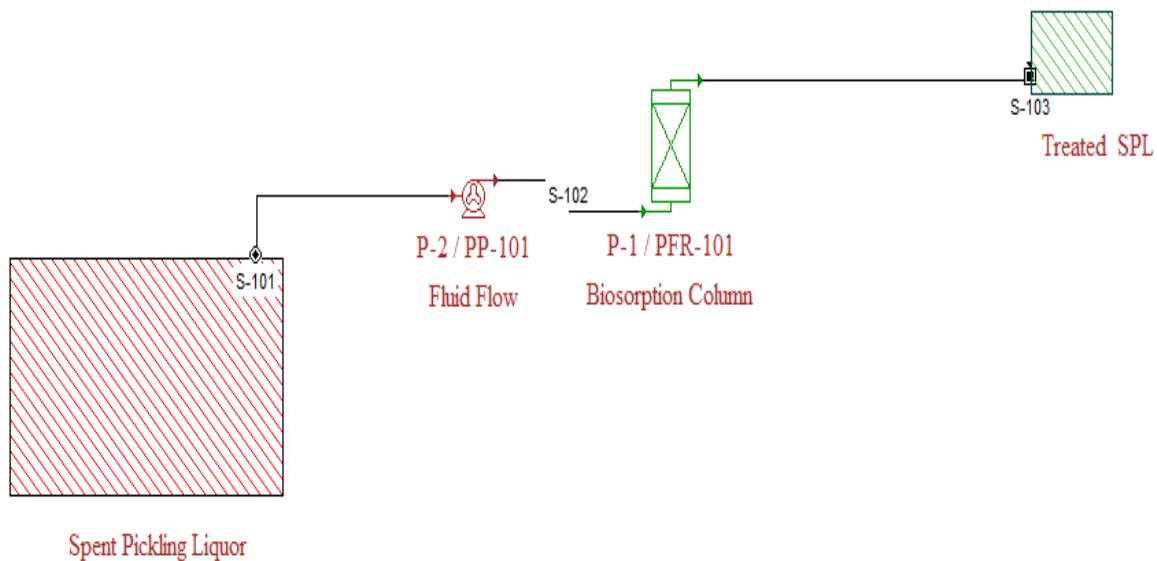


Figure 3.15: Flow diagram of continuous biosorption study

Saturation time (t_{sat} , min) is usually considered when the effluent concentration remains close to influent concentration ($C/C_0 = 0.99$) for a long period.

The uptake capacity (q_e , mg/ g) was obtained by dividing the quantity of Fe (II) biosorbed (m_e) by the biosorbent mass (m) in Equation 3.15 (PerezMarin et al., 2010).

$$q_e = \frac{m_e}{m} \tag{3.15}$$

Where the total quantity of Fe (II) biosorbed in the column (m_e , mg) is calculated from the area above the breakthrough curve multiplied by the inlet concentration and the flow rate (Q , l/min) in Equation 3.16 (PerezMarin et al., 2010).

$$m_e = Q * C_0 * \int_0^{t_b} 1 - \frac{C}{C_0} dt \tag{3.16}$$

All batches and continuous experiments were conducted in triplicate and the means values are presented with a maximum deviation of 8% in all cases performed.

3.6.3 Thomas model

Rigorous fixed bed models usually cast in the form of partial differential Equations, allow a realistic mathematical description of the biosorption column dynamics. When the equilibrium relationship is linear, an analytical solution for the fixed bed dynamic behavior can always be obtained. For nonlinear systems, the governing Equations are usually solved numerically. The Thomas model gives a general analytical solution for these Equations and the assumption of nonlinear equilibrium relationship of Langmuir isotherm. Thomas model neglects the axial dispersion. Thomas model is employed by many researchers to predict the breakthrough curves for biosorption (Travieso et al., 2010).

Thomas model (Thomas, 1944) provides a general analytical solution with the help of a graph between volume and the log of neutralized concentration. Equation 3.17 gives represent standard form and Equation 3.18 linear form.

$$\frac{C_e}{C_0} = \frac{1}{1 + \exp\left[\frac{K_t}{Q}(q_0 M - C_0 V)\right]} \quad (3.17)$$

$$\left(\ln \frac{C_e}{C_0} - 1\right) = \frac{K_t q_0 M}{Q} - \frac{K_t C_0}{Q} V \quad (3.18)$$

where C_e , C_0 = the effluent and influent concentrations of adsorbate in influent (mg/l), q_0 = the maximum adsorption capacity (mg/g), M = the total mass of the adsorbent (g), Q = volumetric flow rate (ml/min), V = the throughput volume (ml) and K_t = the Thomas rate constant (ml/min/mg).

3.6.4 Yoon–Nelson model

The Yoon–Nelson is based on the assumption that the rate of decrease in the probability of biosorption for each biosorbate molecule is proportional to the probability of biosorbate adsorption and the probability of biosorbate breakthrough on the adsorbent. The Yoon–Nelson model not only is less complicated than other models, but also requires no detailed data concerning the characteristics of biosorbate, the type of biosorbent, and the physical properties of the biosorption bed (Han et al., 2009). The Yoon–Nelson equation for a single component system is expressed as Equation 3.20

$$\frac{\ln C_e}{C_0 - C_e} = k_{YN} t - \tau k_{YN} \quad (3.20)$$

Where k_{YN} (l/min) is the rate velocity constant, τ (min) is the time required for 50% biosorbate breakthrough.

3.7 Results and Discussions

Bioremediation is a procedure that utilizes a native or mutated form of biomass for the removal of toxicants from waste (Yoshida et al., 2006; Monteiro et al., 2011). Recently more emphasis has been made to the choice of an efficient biomass that can be employed in repeated cycles of metal removal with minimum or no destruction. Literature shows that microalgae growing naturally in the metal polluted habitats have proved to be the better candidate for this purpose. Such biomass has potential to survive at higher concentration of toxicants, which may otherwise be lethal to the organism. Biosorption is largely influenced by pH, the concentration of biomass, the time of reaction and the interaction between different metallic ions (Ramalina, 2009). Spent pickling was treated with different low-cost agriculture waste (Wheat and Rice husk, Sawdust and banana leave) and microalgae *Scenedesmus* Sp.

Unfortunately, none of the agricultural waste able to treat the SPL may be due to high compaction (Richard and Reynolds, 2009) and the results are tabulated in Annexure F. Further, microalgae (*Scenedesmus* Sp.) was tried to treat the SPL. The *Scenedesmus* sp. was selected for treatment process because research shows that it has potential for treatment of domestic wastewater, Zinc and Cadmium loaded industrial wastewater (Sarwa and Verma, 2014; Monteiro et al., 2011).

3.7.1 Batch biosorption experiments

SPL characteristic is given in Table 3.3. The results show that the pH of the SPL is less than one and Fe concentration is 5 g/l. The sample B and artificial sample have same pH and Fe concentration. Biosorption treatment depends upon the pH, initial metal concentration, and adsorbent dose. Hence, the process parameters are optimized for the batch biosorption study.

3.7.1.1 Effect of pH

It is well known that pH is one of the parameters that play a foremost role in the biosorption of metals with biosorbents, as it determines the surface chemistry of the biomass and metal ion speciation (Bishnoi, 2004). Therefore, the effect of pH on the removal of Fe from SPL solutions was studied by varying pH range from 1 to 7 (Figure 3.16). The results showed that

acidic pH (1–3) did not support significant Fe (II) sorption by the microalgae and biosorption increased almost linearly with increasing pH > 3 and attained maximum value at pH 6. The minimum biosorption of Fe at acidic conditions can be attributed to protonation of active sites of biomass, leading to the generation of electrostatic repulsive forces between metal ions and active sites (Mishra et al., 2010). The increase in uptake of Fe (II) ions with increasing pH could be due to deprotonation of metal binding sites and negative charge density on active sites. A further increase in pH (7) showed a decline in Fe (II) uptake could be due to the conversion of Fe (II) ions to Fe hydroxide [Fe (OH)₂] ensuing into hydroxide precipitation (Toy et al., 2010).

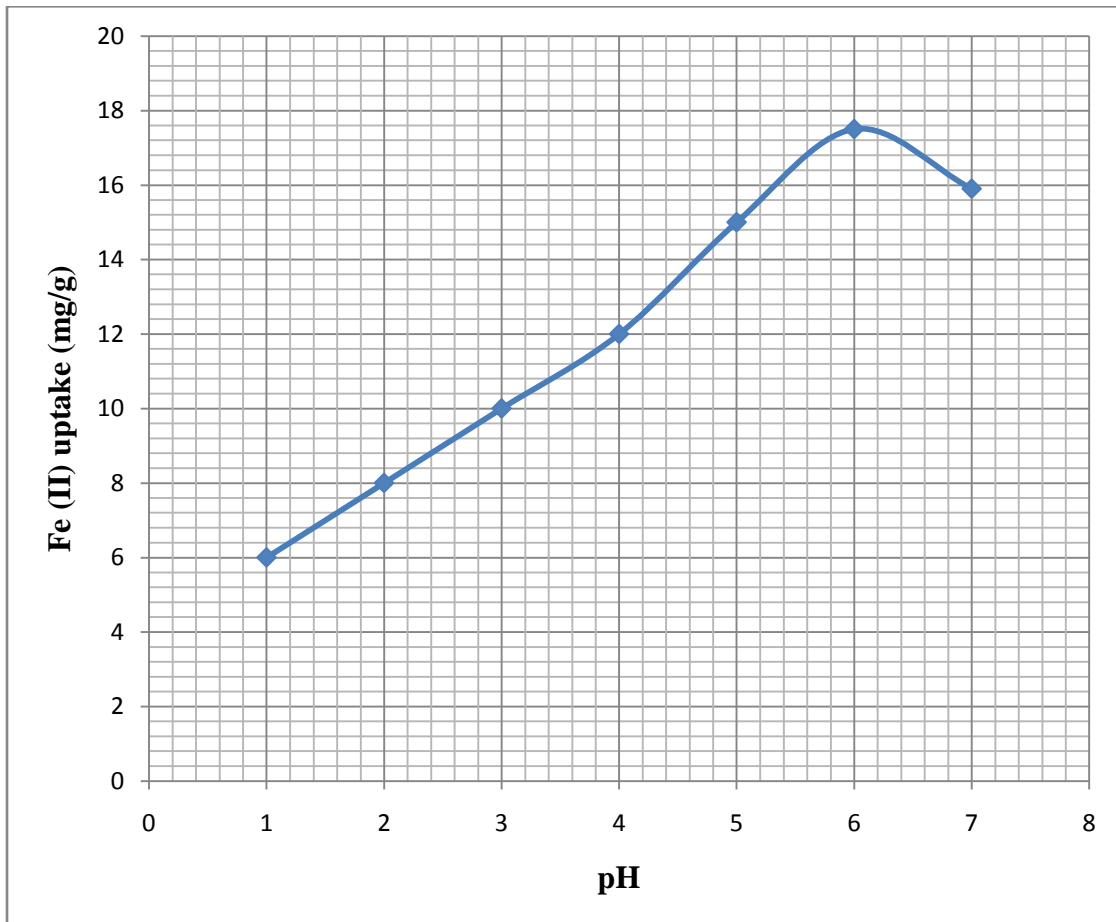


Figure 3.16: Effect of pH on Fe (II) uptake by microalgae
(pH 1-7, agitation rate 200 rpm, Fe (II) concentration 50 ppm, temperature 25-28 °C and sampling at every 10 min)

3.7.1.2 Effect of adsorbent dose

The effect of adsorbent dose on Fe (II) biosorption onto microalgae was examined by varying biomass concentration of 0.125 g, 0.25 g, 0.5 g, 0.75 g, 1 g, 1.5 g and 2.0 g (Figure 3.17). The results show that the biosorbent dose strongly affects the removal of metal. Increase in biosorbent amount (0.125 to 1g) resulted in a great increase in the percentage of Fe (II) uptake. The degree of biosorption of metal ions increases with the increase in biomass concentration because of the increment in the overall surface area of the biosorbent, which, in turn, increases the number of binding sites (Perez-Marín et al., 2009). Any further increase in biomass concentration above 1.0 g/l did not lead to a significant improvement in biosorption yield due to saturation of the adsorbent surface with Fe (II) ions.

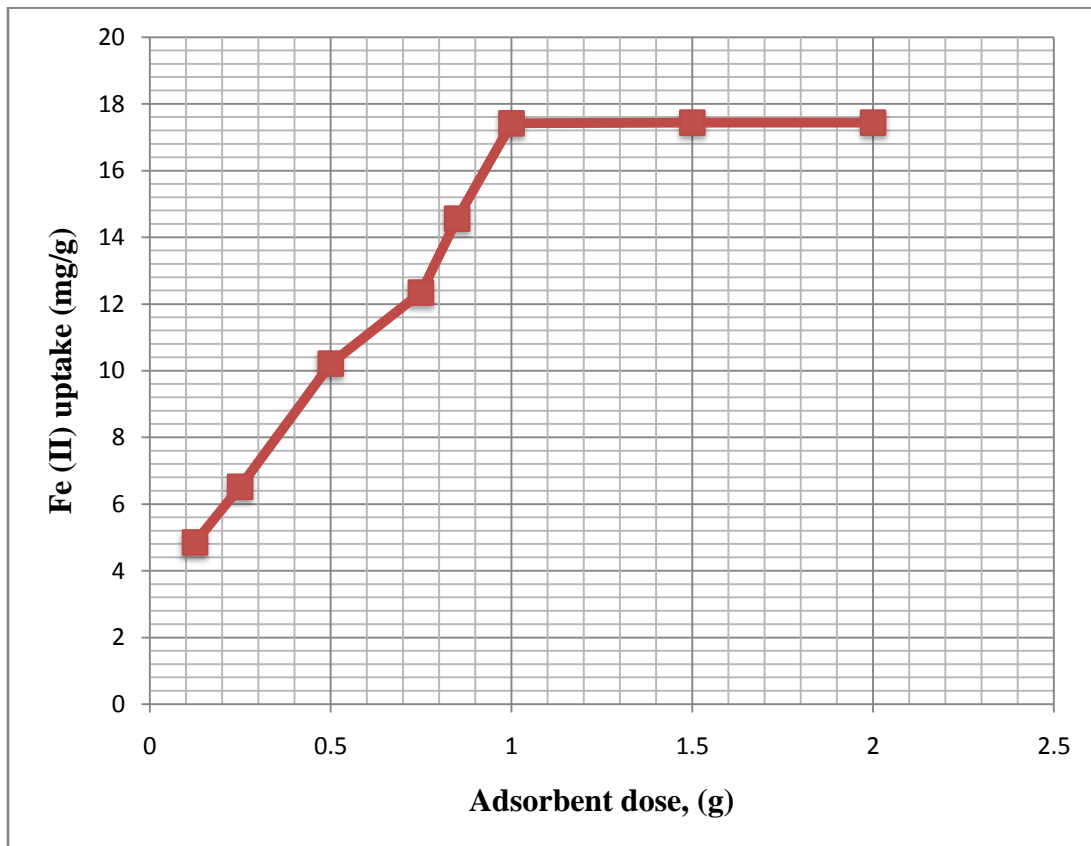


Figure 3.17: Effect of adsorbent dose on Fe (II) uptake by microalgae (pH 6, agitation rate 200 rpm, Fe (II) concentration 50 ppm, temperature 25-28 °C and sampling at every 10 min)

The biosorption performance of a given biosorbent is decided by the metal uptake capacity and removal efficiency. Therefore, a biosorbent dose of 1 g/l was selected for further studies, as it showed comparatively good removal efficiencies and uptake capacities

3.7.1.3 Effect of contact time and initial metal ion concentration

Figure 3.18 shows the effect of contact time and initial Fe(II) ion concentration on biosorption of Fe (II) by *Scenedesmus* sp. In the present analysis, a duration of 180 min was followed out to calculate the equilibrium contact time and it is evident that >50% of Fe (II) was occupied by the biomass within initial 10 min of incubation followed by slower biosorption up to 60 minutes. After 60 min of contact, the amount of biosorbed Fe (II) did not change significantly representing saturation of functional groups on the surface of the microalgae biomass. It can be seen in Figure 3.18, the biosorption of Fe (II) increased from 17 to 79 mg/g by increasing the concentration of Fe (II) in the solution from 50 to 400 mg/l at pH 6 after 60 min of contact time with microalgae.

Figure 3.18 shows the effect of contact time and initial Fe(II) ion concentration on biosorption of Fe (II) by *Scenedesmus* sp. In the present analysis, a duration of 180 min was followed out to calculate the equilibrium contact time and it is evident that >50% of Fe (II) was occupied by the biomass within initial 10 min of incubation followed by slower biosorption up to 60 minutes. After 60 min of contact, the amount of biosorbed Fe (II) did not change significantly representing saturation of functional groups on the surface of the microalgae biomass. It can be seen in Figure 3.18, the biosorption of Fe (II) increased from 17 to 79 mg/g by increasing the concentration of Fe (II) in the solution from 50 to 400 mg/l at pH 6 after 60 min of contact time with microalgae.

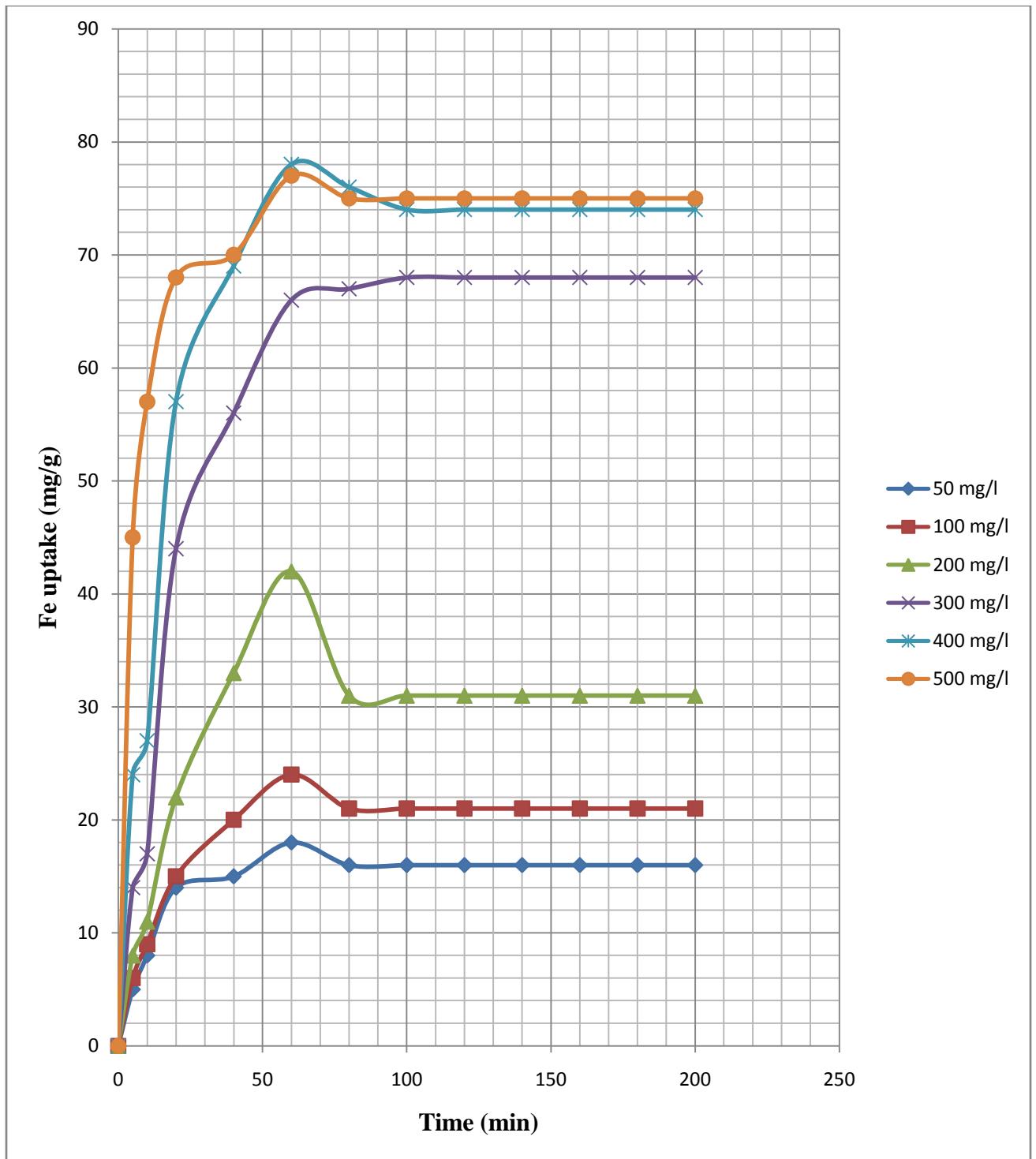


Figure 3.18: Effect of contact time and initial Fe (II) ion concentration
 (pH 6, agitation rate 200 rpm, Fe (II) concentration 50 to 500 ppm, temperature 25-28 °C and sampling at every 10 min)

3.7.1.4 Biosorption kinetics

Kinetic experiments provide the fundamental information about the rate at which biosorption process takes place. Biosorption rate is a useful information for the design of a biosorber. Figure 3.19 and Figure 3.20 depict the experimental kinetic profiles of Fe biosorption fitting to kinetic models (pseudo-first and pseudo-second-order).

The characteristic parameters of the studied kinetic models and their corresponding regression coefficients are tabulated in Table 3.11.

By analyzing the Figure 3.19 and Figure 3.20, the results show that pseudo-second-order model provides an acceptable correlation of the data for all the cases studied ($r^2 > 0.99$).

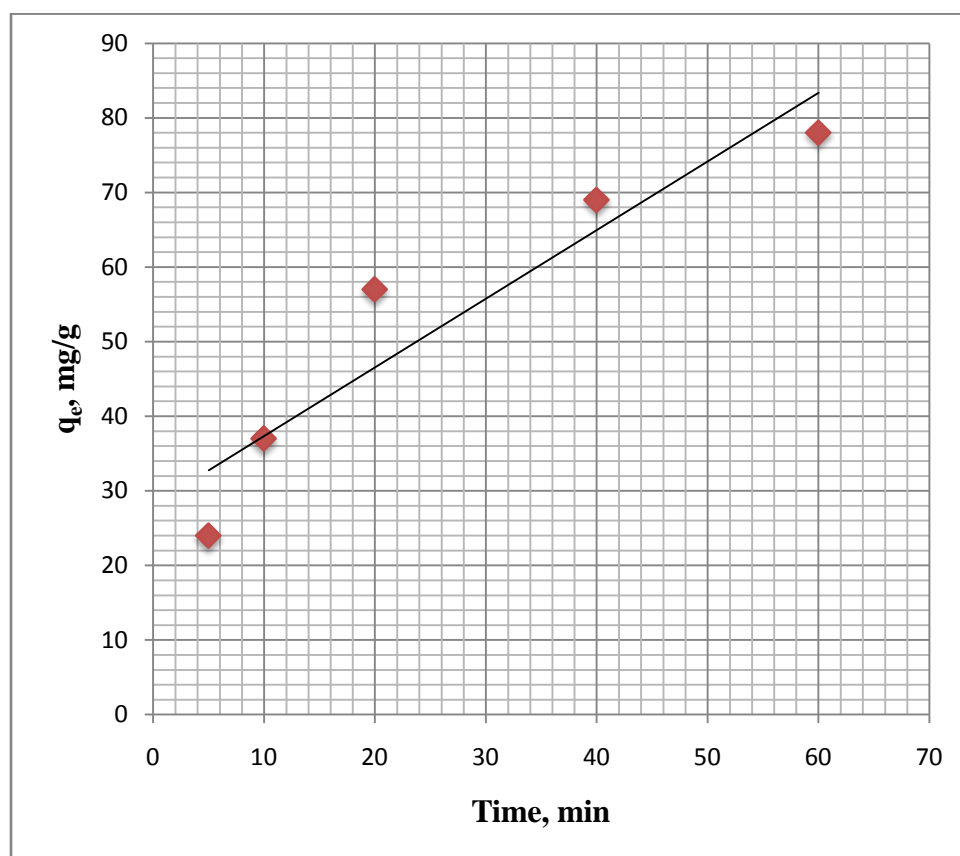


Figure 3.19: Pseudo first-order plot for the biosorption of Fe (II) by microalgae (pH 6, agitation rate 200 rpm, Fe (II) concentration 400 ppm, temperature 25-28 °C, microalgae dosage 1g/l and sampling at every 10 min)

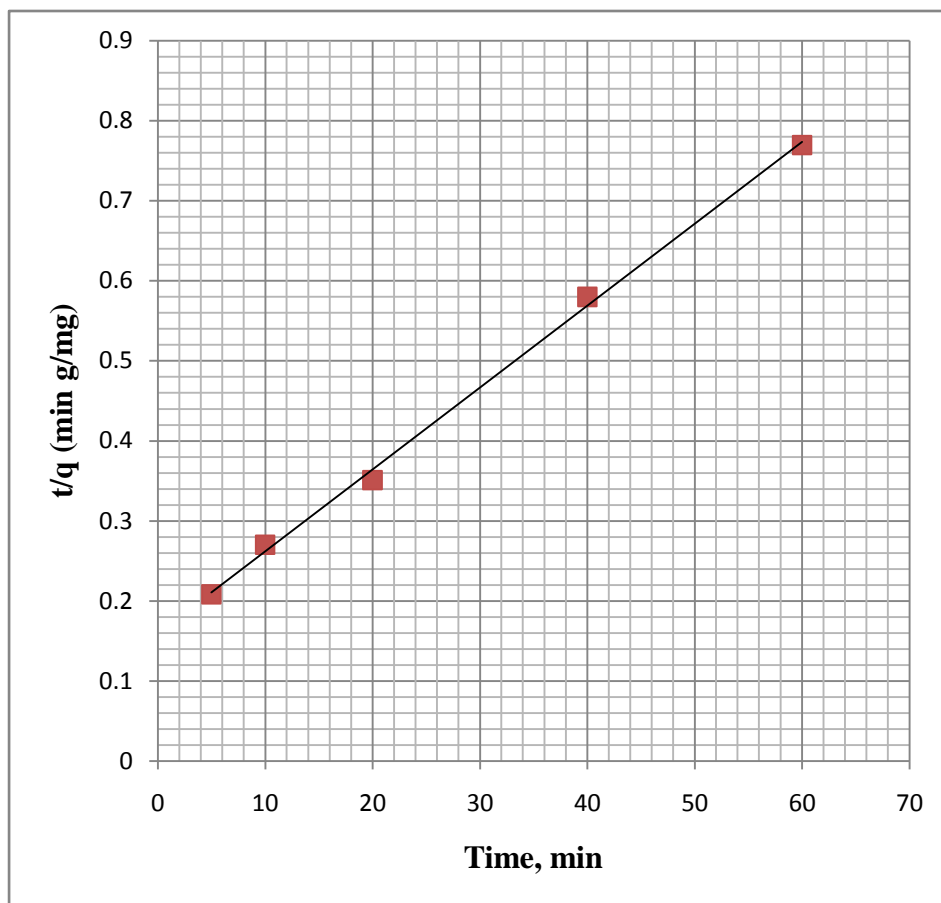


Figure 3.20: Pseudo Second-order plot for the biosorption of Fe (II) by microalgae (pH 6, agitation rate 200 rpm, Fe (II) concentration 400 ppm, temperature 25-28 °C, microalga dosage 1g/l and sampling at every 10 min)

Table 3.12: Characteristic parameter of the studied kinetic models and the regression coefficients

Parameters	First order	Second order
q_e	23.66 (mg/g)	74.78 (mg/g)
K	0.2945 /min	0.0125 (g/mg min)
r^2	0.8842	0.9982

3.7.1.5 Biosorption isotherms

Biosorption isotherms models are useful for finding out the metal binding behavior on the surface of adsorbent and in evaluating the biosorption capacity of adsorbent at equilibrium as a function of its concentration. The equilibrium data obtained for Fe (II) biosorption on algal

biomass was applied on Langmuir and Freundlich Isotherm models in order to investigate the suitable model to represent the adsorption process (Wang and Chen, 2009). In the present investigation, Langmuir and Freundlich's isotherms have been applied on Fe (II) biosorption data to understand the suitability of the process. The applicability of the fit of the curves obtained through the isotherm models was evaluated in terms of linear regression coefficient (r^2).

Performance of *Scenedesmus* sp. for Fe (II) biosorption was achieved by measuring biosorption equilibrium at an initial concentration of 0–500 mg/L within 60 min of contact time and at pH 6. The results obtained after plotting C_e/q_e versus C_e are shown in Figure 3.21, which depicts the relationship of the amount of Fe(II) adsorbed (mg/g) by microalgal biomass and the residual Fe (II) ion concentration. The data were found to fit well with Langmuir model with the maximum biosorption capacity (q_{max}) 142.85 mg/g and $r^2 = 0.973$, respectively. Obtained data through Langmuir isotherm represents monolayer formation of iron ions on the microalgal surface and is not dependent on adjacent site (Volesky, 2001).

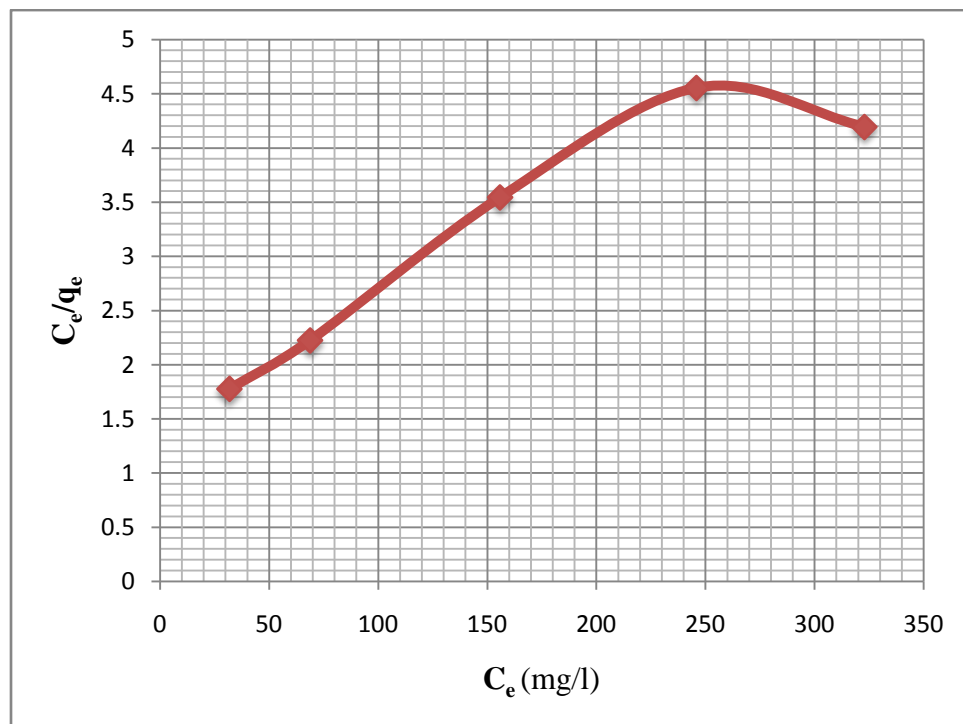


Figure 3.21: Langmuir Isotherm for biosorption of Fe (II) by microalgae for (pH 6, biosorbent dosage 1 g/l and concentration 50 to 500 mg/l)

Figure 3.22 represents the results obtained by a linear form of Freundlich Equation for Fe (II) biosorption by *Scenedesmus* sp. Table 3.13 shows the Langmuir and Freundlich adsorption isotherm constants for Fe (II) biosorption by *Scenedesmus* sp. The magnitude of biosorption capacity ($K = 1.43$) and biosorption intensity ($n = 1.179$) represents high uptake of Fe (II) ions from solution by microalgal biomass (Oves et al., 2013). The high value of n and correlation coefficient (0.992) indicated Fe (II) ions were favorably biosorbed by microalgal cells and Freundlich isotherm fitted well to present study of Fe (II) biosorption. Freundlich isotherm data showed multilayer deposition of iron ion species on the algal surface (Hamdaoui and Naffrechoux 2007).

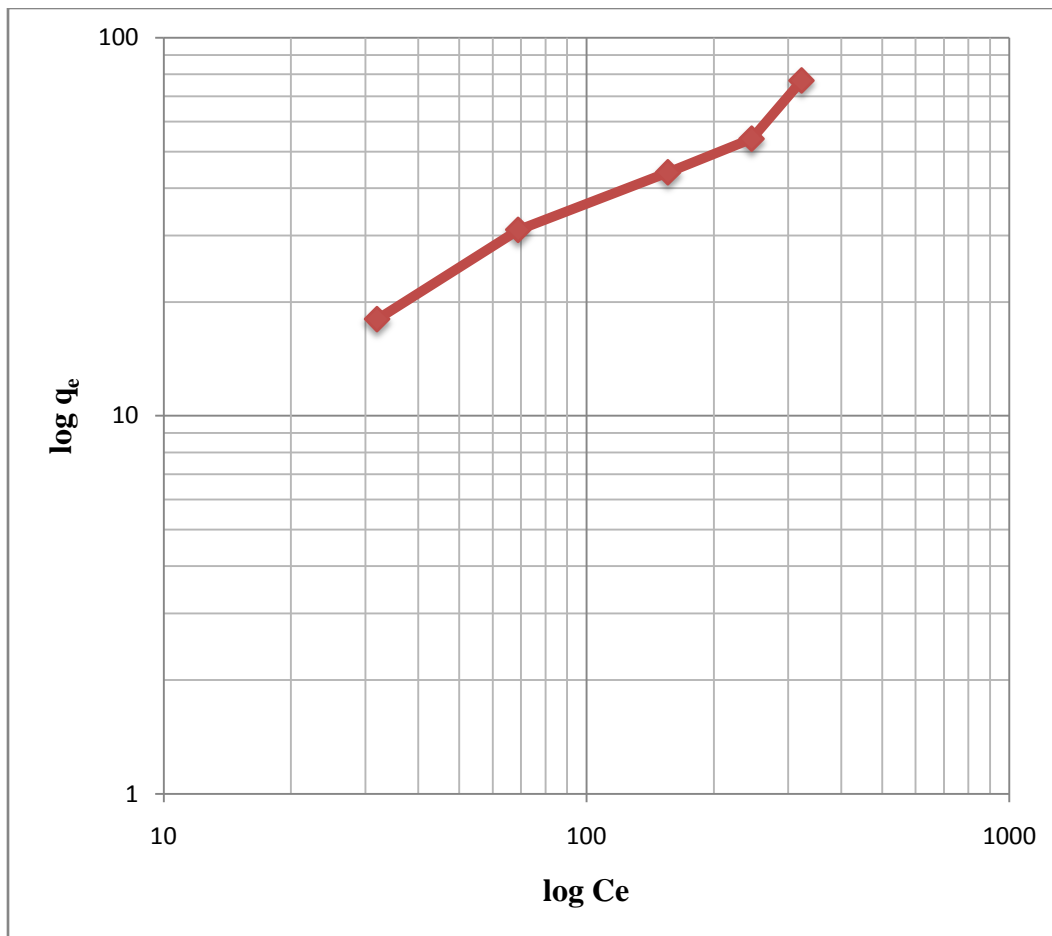


Figure 3.22: Freundlich Isotherm for biosorption of Fe (II) by microalgae
(pH 6, biosorbent dosage 1 g/l and concentration 50 to 500 mg/l)

Table 3.13: Characteristic parameters of the studied isotherm models and the regression coefficients

Metal ion	Langmuir Isotherm			Freundlich Isotherm		
	q_{\max} (mg/g)	b (l/mg)	r^2	K	n	r^2
Fe (II)	142.85	2.534	0.973	1.43	1.179	0.992

3.7.2 Continuous biosorption experiments

Batch biosorption results provide the primary information related to the iron biosorption performance of microalgae. Nevertheless, a continuous mode of procedure is much preferred in industrial effluent treatment plants. Since the successful design of a column absorption process requires the prediction of the concentration-time profile, several mathematical models have been used to describe the fixed bed biosorption (Ghimire, 2003). The Thomas and Yoon-Nelson models were applied in this study to identify the operation of the fixed bed adsorption because they are simple and widely used (Sherman et al., 2016; Elham et al., 2016).

The experimental breakthrough curves (Figure 3.23), at three initial iron concentrations ($C_{20} = 20$ mg/l, $C_{50} = 50$ mg/l, $C_{100} = 100$ mg/l) in solution, and those held by the Thomas model and Yoon-Nelson model are depicted in Figure 3.24 and Figure 3.25 respectively. Experimental breakthrough time (the position at where Fe concentration is 3 mg/l), saturation time (the position at $C/C_0 = 0.99$), and Fe (II) uptake (mg/g), as considerably as the Thomas model parameters and the corresponding regression coefficients, are presented in Table 3.14.

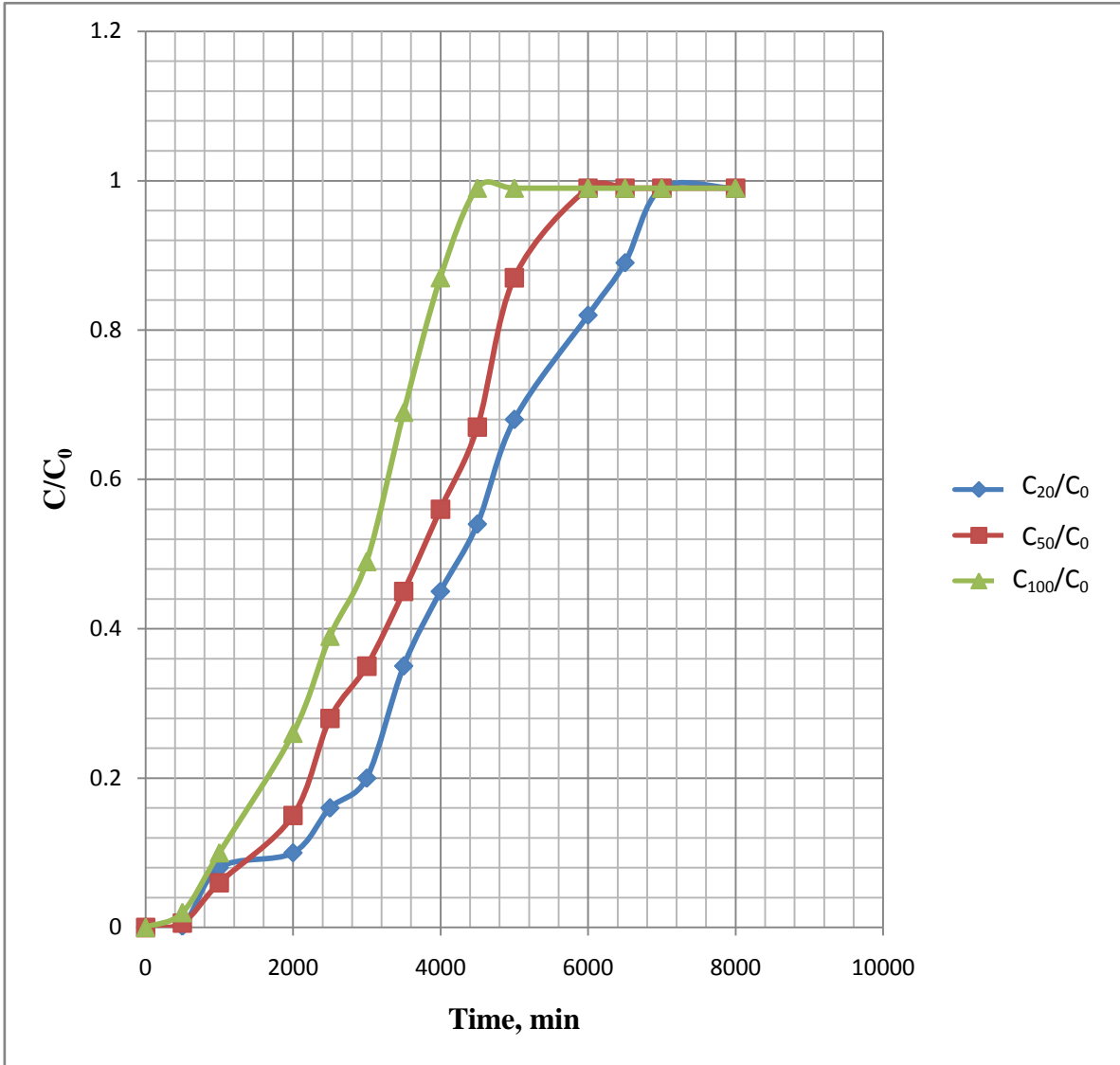


Figure 3.23: Breakthrough curve for biosorption of Fe (II) on microalgae in continuous studies

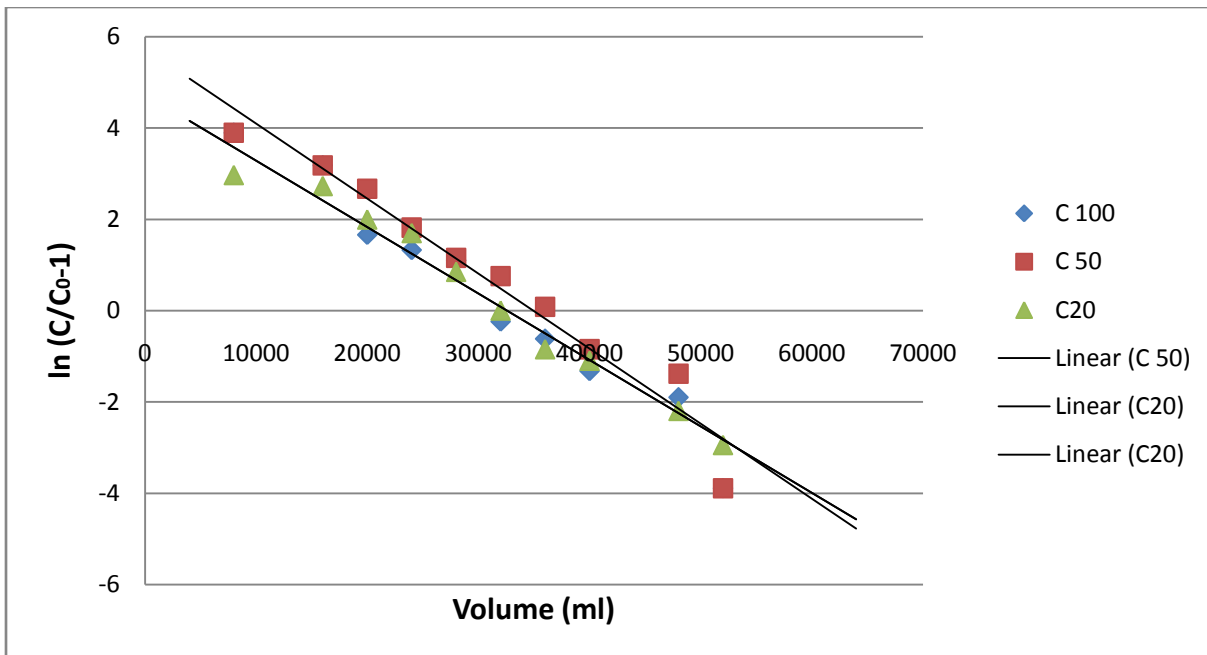


Figure 3.24: Thomas model for biosorption of Fe (II) on microalgae in continuous studies

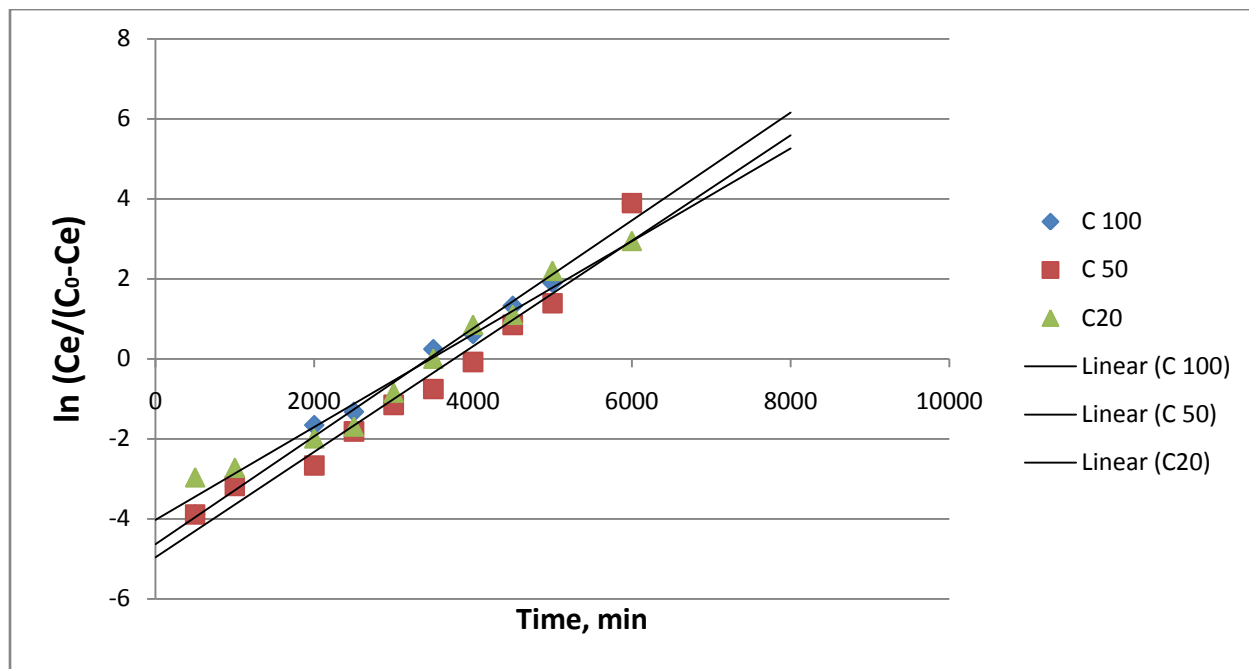


Figure 3.25: Yoon-Nelson model for biosorption of Fe (II) on microalgae in continuous studies

The concentration profiles of the solution leaving the column showed that the biosorption zone, the portion of the column where biosorbate is transferred to the biosorbent, travels through the tower and finally coincides with the height of the tower. At this moment, the metal ion concentration gradually increases just to reach the feed concentration. Iron removal is fast and highly effective during the initial stage. Subsequently, metal removal decreases, as an effect of the progressive saturation of the binding sites. The breakthrough time and the saturation time decrease as the initial iron solution concentration increases, due to the fast saturation of the binding sites (Chu et al., 1997).

From the results (Fig. 3.24, 3.25 and Table 3.14), it was observed that the two tested models (Thomas model and Yoon–Nelson model) were able to describe the column data well with high correlation coefficients (> 0.98).

The Thomas model is one of the models most widely used in describing column performance. The suitability of the Thomas model may be elucidated that this model assumes negligible axial dispersion in the column adsorption since the rate driving force obeys second-order reversible reaction kinetics. The biosorption is control by mass transfer at the interface and not limited to the chemical reaction (Biswas and Mishra, 2015). The Thomas model constant K_t increased with increasing influent metal concentration.

A simple theoretical model developed by Yoon–Nelson was used to investigate the breakthrough behavior of Fe (II) on microalgae. The model constant k_{YN} (a rate constant) and τ (the time required for 50% sorbate breakthrough) could be obtained. The values of k_{YN} and τ are presented in Table 3.14. The time required for 50% sorbate breakthrough with this model agreed very well with the experimental data. The model constant k_{YN} increased with increasing influent metal concentration, which indicates that sharper breakthrough curves were obtained at higher influent metal concentration.

Table 3.14: Experimental parameters of the breakthrough curves and characteristic parameters of the Thomas model and Yoon-Nelson model with their corresponding values of the regression coefficient (r^2).

Breakthrough Curve			
Initial Fe concentration (mg/l)	t_b (min)	t_{sat} (min)	
20	2856	6800	
50	879	5980	
100	558	4150	
Thomas Model			
Initial Fe concentration (mg/l)	q_o (mg/g)	K_t (ml/min/mg)	r^2
20	39.79	4.23	0.981
50	61.45	5.45	0.984
100	156.85	6.32	0.987
Yoon–Nelson Model			
Initial Fe concentration (mg/l)	k_{YN} (l/min)	τ (min)	r^2
20	69	3750	0.983
50	138	2741	0.985
100	176	1890	0.988

3.7.3 FTIR analysis

In order to determine which functional groups were responsible for metal uptake, FTIR spectra of the biosorbent before and after Fe (II) bonding were recorded. The spectra of biosorbent were measured in the range of 400 – 4000 cm^{-1} . As can be seen in Figure 3.26, the spectra show a number of absorption peaks, indicating the complex nature of the material studied.

The change observed in the spectrum indicates the possible involvement of different functional groups of algae in Fe (II) biosorption process. The FTIR transmittance of the *Scenedesmus* sp. algal species (Figure 3.27) reveals the presence of –OH, –COOH, NH_2 , and CO organic compound groups (Aliphatic character: 400–800 cm^{-1} ; Phenols and alcoholic

group: 1,000–1,400 cm^{-1} ; Carboxyl group: 1,500–1,700 cm^{-1} and Hydroxyl group: 3,200–3,400 cm^{-1} .

Comparing the spectra before and after sorption of metal ions, differences in the position of the absorbance peaks were observed which indicates the involvement of Hydroxyl and amine groups for iron adsorption.

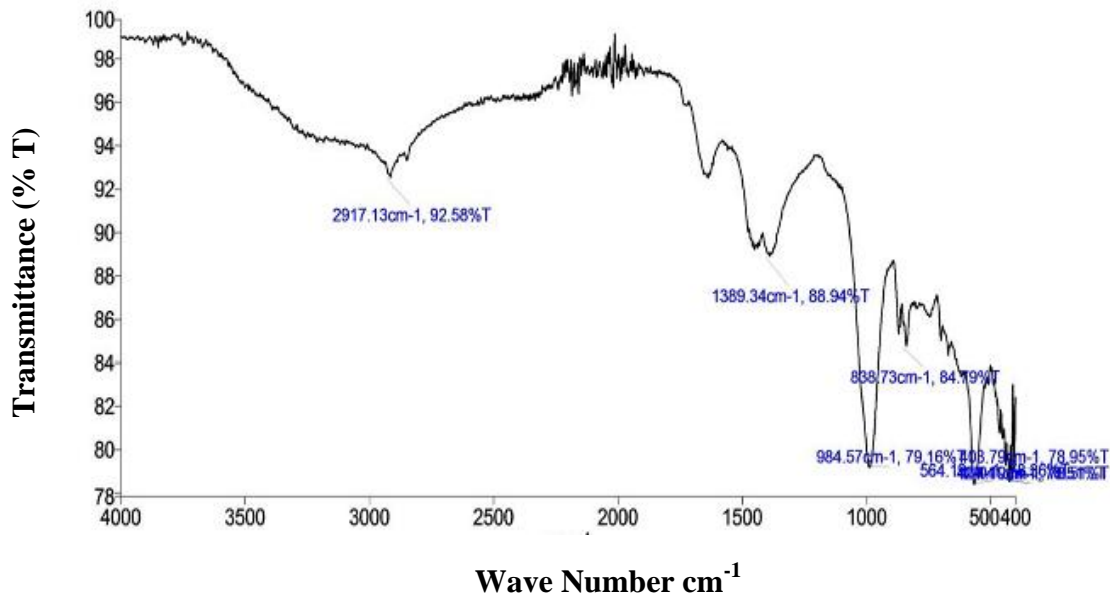


Figure 3.27: FTIR spectrum of unused microalgae

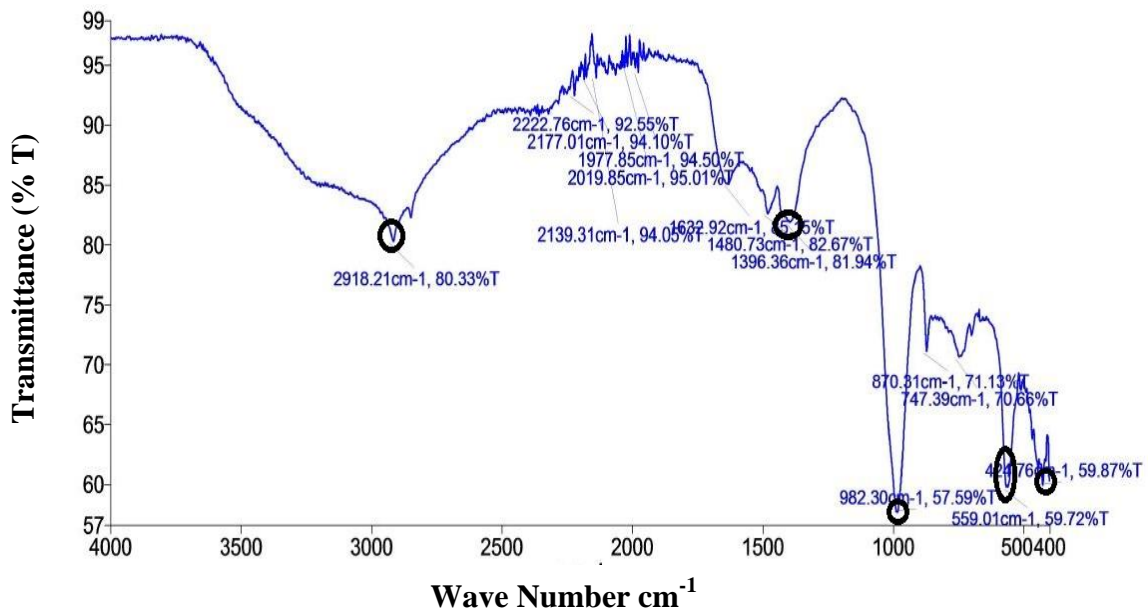


Figure 3.28: FTIR spectrum of used microalgae

3.8 Discussions

The SPL was trying to treat with the biosorption method because it has many advantages over chemical methods. The low-cost adsorbents, such as agricultural wastes (wheat husk, banana leaves, rice husk and sawdust) and microalgae (*Scenedesmus* sp.) were used for the study due to their local availability. Unfortunately, none of the agricultural waste was able to treat the SPL. The observational results show that the microalgae could be considering a potential biosorbent for the removal of iron from SPL. Iron biosorption is strongly affected by parameters such as biosorbent dose, initial iron concentration, contact time and pH of the solution. The biosorbent dose was varying from 0.125 g to 2 g, iron concentration from 50 to 500 ppm, contact time from 0 to 180 min and pH from 1 to 7 for the batch study respectively. The results of the batch study show that the metal removal increased with increase in biosorbent dose and pH solution. The optimum adsorbent dose is 1gm/l at 6 pH is due to deprotonation of metal binding sites and negative charge density on active sites (Mishra et al., 2010). Kinetic studies show that iron biosorption on microalgae surface took approximately 1 hour to reach equilibrium. Observational data can be described adequately by the pseudo-second-order kinetic confirming the chemisorption of iron on the algal surface. The experimental isotherms data were analyzed using Freundlich and Langmuir equations. The best fit was obtained by Freundlich isotherm with high correlation coefficients. The magnitude of biosorption capacity ($K = 1.43$) and biosorption intensity ($n = 1.179$) represents high uptake of Fe (II) ions from solution by microalgal biomass (Oves et al., 2013). Freundlich isotherm data showed multilayer deposition of iron ion species on the algal surface (Hamdaoui and Naffrechoux 2007). In multilayer adsorption, the stronger binding sites are occupied first, until adsorption energy is exponentially decreased upon the completion of adsorption process (Aravantinou et al., 2013). Batch biosorption results provide the primary information related to the iron biosorption performance of microalgae. However, a continuous mode of procedure is much preferred in industrial effluent treatment plants. Continuous biosorption study was performed from for the three different initial concentrations of solution (20 mg/l, 50 mg/l, and 100 mg/l). The continuous biosorption studies revealed that microalgae (*Scenedesmus* sp.) could be successfully used as biosorbent for treating SPL containing Fe (II) ions. The Thomas and Yoon-Nelson models are successful

in describing the breakthrough curves. FTIR analysis of the biosorbent, before and after iron sorption, shows that amine and hydroxyl groups could be involved in metal binding to the microalgae biomass.

References

- Aravantinou, A.F., Theodorakopoulos, M.A., Manariotis, I.D.(2013). Selection of microalgae for wastewater treatment and potential lipids production. *Bioresour. Technol.*, 147: 130–134.
- Banu JR, Khac UD, Kumar SA, Ick-Tae Y, Kaliappan S (2012). A novel method of sludge pretreatment using the combination of alkalis. *Journal of Environmental Biology*, 33(2):249-53
- Bishnoi NR, Bajaj M, Sharma N and Gupta A (2004). Adsorption of Cr(VI) on activated rice husk carbon and activated alumina. *Bioresour Technol*, 91: 305 – 307.
- Biswas Swarup and Mishra Umesh (2015). Effective Remediation of Lead Ions from Aqueous Solution by Chemically Carbonized Rubber Wood Sawdust: Equilibrium, Kinetics, and Thermodynamic Study. *Journal of Chemistry*, 2015:1-8.
- Brar Satinder Kaur, Jyoti Sarma Saurabh, Kannan Pakshirajan (2010). *Platform Chemical Biorefinery: Future Green Chemistry Elsevier, Cambridge, USA, Page No. 141, ISBN:978-0-12-802980-0.*
- Boris Stepanovich Maslov (2009). *Agricultural Land Improvement: Amelioration and Reclamation, Singapore, Vol. 2, Page No.476, ISBN: 978-1-84826-549-3.*
- Chu K. H., Hashim M. A., Phang S. M., Samuel V. B. (1997). Biosorption of Cadmium by Algal Biomass: Adsorption and Desorption Characteristics, *Water Science Technology.*, 35 (7): 115–122.
- Elham Cheraghi, Elham Ameri, Ahmad Moheb (2016). Continuous biosorption of Cd(II) ions from aqueous solutions by sesame waste: thermodynamics and fixed-bed column studies. *Desalination and Water Treatment*, 57(15): 6936-6949.

Ghimire KN, Inoue K, Yamaguchi H, Makino K and Miyajima T (2003). Adsorptive separation of arsenate and arsenite anions from aqueous medium by using orange waste. *Water Resource*, 37: 4945 – 4953.

Hamdaoui O, Naffrechoux E (2007). Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon. Part I. Two-parameter models and equations allowing determination of thermodynamic parameters. *Journal of Hazardous Material*, 147(1-2): 381-94.

Hana Runping, Yu Wanga, Zhao Xin, Wang Yuanfeng, Xie Fuling, Cheng Junmei, Tang Mingsheng (2009). Adsorption of methylene blue by phoenix tree leaf powder in a fixed-bed column: experiments and prediction of breakthrough curves. *Desalination*, 245: 284–297.

IS 4032:1985, Indian Standard Method of chemical analysis of hydraulic cement (2004). Bureau of Indian Standard, New Delhi.

Langmuir I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of American Chemical Society*, 40: 1361-1403.

Marín AB Pérez, Aguilar MI, Ortuño JF (2010). Biosorption of Zn (II) by orange waste in batch and packed-bed systems. *Journal of Chemical Technology Biotechnology*, 85: 1310–1318.

Mishra Vishal, Balomajumder Chandrajit, Agarwal Vijay Kumar (2010). Zn (II) Ion Biosorption onto Surface of Eucalyptus Leaf Biomass: Isotherm, Kinetic, and Mechanistic Modeling, *Clean – Soil, Air, Water*, 38(11): 1062–1073.

Monteiro C., Castro P. L., Malcata F. X (2011). Capacity of Simultaneous Removal of Zinc and Cadmium from Contaminated Media, by Two Microalgae Isolated from a Polluted Site. *Environmental Chemical Letter*, 9 (4): 511–517.

Oves Mohammad, Khan Mohammad Saghir, Zaidi Almas (2013) Biosorption of heavy metals by *Bacillus thuringiensis* strain OSM29 originating from industrial effluent contaminated north Indian soil, *Saudi Journal of Biological Sciences*, 20(2): 121–129.

Pérez Marín AB, Aguilar MI, Ortuño JF (2010). Biosorption of Zn(II) by orange waste in batch and packed-bed systems. *Journal of Chemical Technology Biotechnology*, 85: 1310–1318.

Perez'-Mar'in AB, Ortuno~ JF, Aguilar MI, Meseguer VF, Saez' J and Llorens' M (2010). Use of chemical modification to determine the binding of Cd (II), Zn (II) and Cr (III) ions by orange waste. *Biochemical Engineering Journal*, 53(1): 2–6.

Ramalina fraxinea (2009). *Biomass. Clean – Soil Air Water*, 37: 249–255.

Reynolds T. D. and Richard P. A. (2009). *Unit Operations and processes in environmental engineering* (2nd ed.). PWS publishing, Toronto, pp. 795.

Rippka, R., Deruelles, J., Waterbury, J.B., Herdman, M. and Stanier, R.Y. (1979). Generic assignments, strain histories and properties of pure cultures of Cyanobacteria. *Journal of General Microbiology*, 111: 1-6.

Sarwa, P. and Verma, S.K. (2014). Recovery and Recycling of Zn (II) from Wastewater of Viscose Fiber Industry by *Scenedesmus* sp. MCC 26 Isolated from a Heavy Metal Contaminated site. *Clean, Air and Soil*, 42: 1-6.

Sharmeen Afroze, Tushar Kanti, H. M. Ang (2016) Adsorption performance of continuous fixed bed column for the removal of methylene blue (MB) dye using *Eucalyptusheathiana* bark biomass. *Research on Chemical Intermediate*, 42 (3): 2343–2364.

Standard Methods for the Examination of Water and Wastewater (1998). 20th Edn. APHA, AWWA, WEF, Washington, DC.

Tay T., Candan M., Erdem M, ,Imen Y., H. Tu`rk (2009). Biosorption of Cadmium Ions from Aqueous Solution onto Non-living Lichen *Ramalina fraxinea* Biomass. *Clean Soil Air Water*, 37 (3): 249–255.

The Gazette of India, Extraordinarily, Part-11, Section 3, Sub-section (ii), published by Authority No. 471, New Delhi, Friday, May 23, 2003, Min. of Environment & Forest, Notification, New Delhi, 20th May, 2003.

Thomas, H. C. (1944). Heterogeneous Ion Exchange in a Flowing System. *Journal of the American Chemical Society*, 66: 1666.

Travieso L., Canizares R. O., Borja R., Benitez F., Dominguez R., Dupeyron R. & Valiente V (1991). Heavy metal removal by microalgae, *Bulletin Environmental Contamination and Toxicology*, 6: 144-151.

Verma S. K., Raveender V., Scaria J, (2002). Application of Mutant Strains of Cyanobacteria for Cd² Removal, *Bull. Environ. Contam. Toxicol.*, 69 (5): 632–637.

Verma S. K. and Singh S. P. (1990). Factors Regulating Copper Uptake in a Cyanobacterium, *Curr. Microbiol.*, 21 (1): 33–37.

Volesky B. (2001). Detoxification of Metal-Bearing Effluents: Biosorption for the Next Century, *Hydrometallurgy*, 59 (2): 203–216.

Wang J., Chen C. (2009). Biosorbents for Heavy Metals Removal and Their Future, *Biotechnol. Adv.*, 27 (2): 195–226.

Yoshida N., Ikeda R., Okuno T. (2006), Identification and Characterization of Heavy Metal-Resistant Unicellular Alga Isolated from Soil and Its Potential for Phytoremediation, *Bioresour. Technol.*, 97 (15), 1843– 1849.

Wentz Charles A., Hazardous waste management, 2 ed., McGraw-Hill, Inc., New Delhi: 1995.

Applications of pickling sludge

This chapter discusses the applications of pickling sludge as fertilizer and in manufacturing of pavement tiles.

4.1 Introduction

In the previous chapter, we saw that a lot of sludge was generated during the treatment of SPL. This method is limited by the growing need for landfills to store the precipitate (Rakhshae et al., 2009). The heavy metals leachate of pickling sludge may contaminate the groundwater. A new approach for remediating heavy metal is through immobilization, which transforms heavy metals into less bio-available forms whilst providing essential plant growth properties in terms of nutrition and water holding capacity (Bolan et al., 2014). Materials that may achieve this include:

- 1) Composts derived from materials such as sewage sludge and other municipal sources (Brown et al., 2003; Hartley et al., 2004).
- 2) Natural or synthetic zeolites; (Cholpecka and Adriano, 1996; Edwards et al., 1999; Gworek, 1992; Haidouti, 1997; Lin et al., 1998) or
- 3) Industrial by-products such as red-mud or other iron-rich materials such as iron grit or iron oxyhydroxides (Brunori et al., 2005; Friesl et al., 2003).

Remediation techniques that utilize waste materials may be cost-effective compared to methods that are more traditional, may effectively divert materials from the waste stream, and could thereby make a dual contribution to sustainable development. With this aim, the possibilities of using waste from metallurgical industries as fertilizers and raw material for pavement tiles were explored to reduce the burden of a disposal problem.

4.2 Investigations on the Feasibility of Utilizing Sludge as Fertilizer

4.2.1 Materials and procedure

Pickling sludge and copper tailing were used as a raw material for improving the fertility of the soil. SPL was treated with lime (commercial grade) as described in the previous chapter and the pickling sludge produced in this process was used for the study. Copper tailing procured from the Hindustan Copper Limited, Khetri (Rajasthan) because the characteristics

of copper tailing (Saxena et al., 2016; Thomas et al., 2012; 2013) showed that it contains metals that may act as micronutrients. Oleander plant was chosen for the study because Pilani environmental conditions are suitable for its growth and it is a non-consumable (ornamental) plant. The chemical characterization of copper tailing and study area soil (Pilani, Rajasthan) was done by XRF and elemental analysis was done in Inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ARCOS from M/s. Spectro, Germany). The oleander plants were planted with four different compositions to study the plant growth. Soil to fertilizer ratio taken for the study was 3:1. Four pots were used for plantation. In the first pot, the plant was planted in soil and organic fertilizer (cow dung). In the same way, in the second pot, soil and copper tailing; in the third pot soil and pickling sludge; and in the fourth pot, soil and pickling sludge along with copper tailing in equal quantity were used. The study was carried out under sun and shadow conditions.

Sample 1 = Soil + organic fertilizer (cow dung) (control Plant)

Sample 2 = Soil + copper tailing

Sample 3 = Soil + pickling sludge

Sample 4 = Soil + pickling sludge and copper tailing with equal ratio.

The effects of heavy metals (present in industrial waste) on plant uptake were analyzed by ICP-AES analysis of plant leaves.

4.2.1.2 Principles of ICP-AES

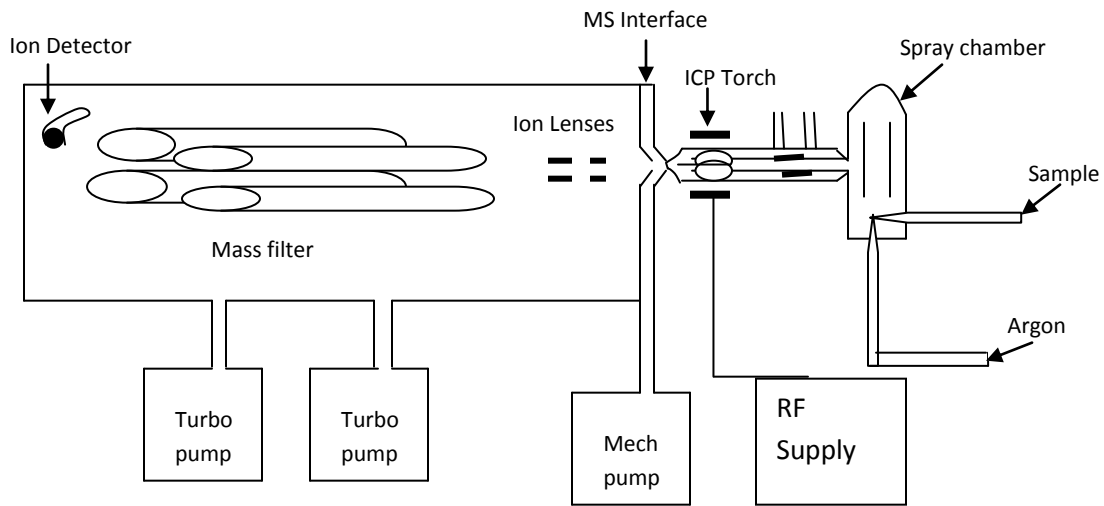


Figure 4.1: Basic components of ICP-AES (Thomas, 2015)

ICP-AES consists of components such as the nebulizer, spray chamber, plasma torch, interface, and detector. Figure 4.1 shows the basic instrumental components that make up an ICP-AES system. The steps involve in ICP-AES are:

- a) Sample nebulized in a spray chamber.
- b) Argon transport sample and sustain the plasma
- c) RF generator supplies energy to induct coil.
- d) Sample atomized and ionized in the plasma
- e) Ions are transmitted through the interface and most of the gas removed
- f) Quadrupole filter the ions by mass
- g) The detector counts the ions

4.2.2 Results and Discussions

4.2.2.1 Characterization of copper tailings and pickling sludge

The pH of the pickling sludge is 7.5 (Table 3.4). The main constituents of pickling sludge are (Table 4.1) CaO, Cl, Mg, Fe₂O₃, and SiO₂, which are vital micronutrients for plant growth (Jones, 1997).

Table 4.1: Pickling sludge characterization

Chemical parameter	Concentration (%)
CaO	71.52
O	26.32
Cl	12.45
MgO	6.19
Fe ₂ O ₃	6.12
SiO ₂	1.87
Al ₂ O ₃	0.4

Copper tailing is in powdered form. Its specific gravity is about 3.14 and contains 99% insoluble (mainly silica) with the very small quantity of other metals (Table 4.2).

Table 4.2: Characterization of Copper tailing

Physico-chemical parameter	Concentration (%)	Physico-chemical parameter	Concentration (ppm)
Cu	0.13	Re	16
Al ₂ O ₃	4.53	Se	0.9
Fe ₂ O ₃	0.96	Cd	1
CaO	0.70	Sn	70
MgO	1.65	Hg	23
K ₂ O	0.70	Fe	36
Na ₂ O	0.15	Pb	17
TiO ₂	0.13	As	81
SiO ₂	83.54	Au	0.18
S	1.31	Mo	9
Sp. Gravity	3.14	Sb	8
Bulk Density, g/ml	1.34	Ni	29
Total Insoluble (aqu)	99.08	Co	40
		Mn	890

Thus, copper tailing and pickling sludge are rich in metals, sand, minerals and have the potential to be used in agriculture as a cheaper source of micronutrients, either in its present form or after suitable processing/refining. Micronutrients play a vital role in the growth and developments of plants & are considered as an essential for increasing crop yields.

Both copper tailing and the sludge possess the elements that can be considered as a nutrient for Plant growth. Hence, a study was carried out to investigate the utility of these industrial wastes as fertilizers in ornamental plant. The soil composition of study area Pilani is given in Table 4.3.

Table 4.3: Chemical composition of soil

Chemical Composition	Concentration (%)	Chemical Composition	Concentration (ppm)
SiO ₂	48.9	Rb ₂ O	92
Al ₂ O ₃	10.23	Cr ₂ O ₃	90
MgO	4.18	NiO	57
Fe ₂ O ₃	4.1	FeO	57
K ₂ O	1.77	Nb ₂ O ₅	38
CaO	1.55	CuO	38
Na ₂ O	0.86	As ₂ O ₃	17
TiO ₂	0.47	Ga ₂ O ₃	14
P ₂ O ₅	0.09		
MnO	0.06		
ZrO ₂	0.05		
BaO	0.05		
SrO	0.02		
SO ₃	0.02		
Cl	0.01		

The growth characteristics of plantations in each sample were compared and the sample with the organic fertilizer was used as a reference value. The recorded heights of the plantations were higher in the presence of sunlight in all the samples than those kept under shadow condition. The recorded plant heights under sun and shadow condition are given in Table 4.4 and 4.5. In the first 2 months, the plants grew slowly and gradually. Whereas in the next 2 months, the plant growth rate was comparatively higher this became stagnant eventually.

The growths of these plants were studied for both environmental conditions viz. shadow and sun conditions. The Sample 2 and Sample 4 exhibit a higher growth in plants as compared to

the Sample 1. The outcomes of plant heights confirm that the copper tailings can be applied as plant nutrients. Sample 3 contained the soil with pickling sludge in which the plant was stunted when kept in the sun and did not survive in the shadow condition. Therefore, the pickling sludge cannot be applied as fertilizer alone. The foremost plant where branches flower and fruits first appeared was Sample 4. The pictures of plant growth are depicted in Annexure G.

Table 4.4: Height of plant under sun condition*

Height of plant (in cm)				
Time (in week)	Sample 1	Sample 2	Sample 3	Sample 4
Initial	28	28	28	28
1	28.5	33	28	29
2	29.3	33	28	29.1
3	35	36.8	28.2	31.2
4	40.6	41.6	28.5	36.2
5	44	46	28.5	40
6	48.8	49.5	29.8	44.5
7	54	55	29.9	48
9	57.5	64	38	54.5
11	65	72.1	43	61
13	67.3	75.1	44.1	63.8
16	68.7	76.6	44.5	64.4
20	68.8	76.8	44.5	64.5
24	69	77	44.5	64.6+31.5 branch
25	69	77	44.5	64.6+31.5 branch+flower

Table 4.5: Height of plant under shadow condition*

Height of plant (in cm)				
Time (in week)	Sample 1A	Sample 2A	Sample 3A	Sample 4A
Initial	28	28	28	28
1	30	31.5	28	33
2	30.5	33	28.5	33.8
3	35.3	39.5	- *	38
4	39.5	44.4	-	40
5	40.5	46.2	-	43
6	41	47.5	-	44
7	42.5	50	-	48
9	46	54.5	-	53.2
11	45	56.5	-	57.5
13	46.3	57.1	-	59.5
16	46.4	58	-	60.4
20	46.5	58.1	-	60.5
24	46.6	58.2	-	60.6
25	46.6	58.2	-	60.6

-* unable to survive

***Under Sunlight**

Sample 1= Blank = soil + fertilizer organic
 Sample 2=Tailing= copper tailing +soil
 Sample 3=Sludge= pickling sludge + soil
 Sample 4=Mix= tailing +sludge

***Under Shadow**

Sample 1A= Blank = soil + fertilizer organic
 Sample 2A=Tailing= copper sludge +soil
 Sample 3A=Sludge= pickling sludge + soil
 Sample 4A=Mix= tailing +sludge

4.2.2.2 Influence of copper tailings

Plants in the sample containing copper tailings as a fertilizing agent showed improved growth. The growth in these samples was greater than the sample with organic fertilizer (cow dung) (Table 4.4 and 4.5).

4.2.2.3 Influence of sludge produced from spent pickling liquor

Pickling sludge caused damage to the plants. The plants under sun condition reduced the growth, whereas those in the shadow condition did not survive may due to high concentration of lime (>78%) and iron content (Table 4.4 and 4.5).

4.2.2.4 Influence of a combination of both copper tailing and sludge

When a combination of both copper tailings and pickling sludge was used, growth was observed to be higher than the organic fertilizers (cow dung) in both shadow and sun conditions (Table 4.4 and 4.5).

Table 4.6: Concentration of metal ions in plants in various treatments

Metal ions	Concentration (in ppm)			
	Sample 1	Sample 2	Sample 3	Sample 4
Al	1702±0.82	2165±0.35	2071±0.39	1937±0.22
As	57±0.21	48±0.81	45±0.51	45±0.28
B	225±0.51	157±0.65	128±0.58	94±0.01
Ba	116±0.64	10±0.47	13±0.01	18±0.71
Ca	12416±0.3	16958±0.40	14898±0.50	14005±0.7
Fe	226±0.73	230±0.85	335±0.55	250±0.47
K	35710±0.9	26525±0.61	41936±0.2	28111±0.60
Mg	4147±0.64	6320±0.99	3817±0.13	4500±0.03
Na	3299±0.53	2589±0.07	3678±0.95	5181±0.79
P	1639±0.96	1173±0.67	1140±0.72	1292±0.90
S	2305±0.03	2675±0.90	1954±0.48	1923±0.59
Si	1274±0.65	517±0.66	787±0.23	548±0.88
Sr	87±0.84	289±0.84	116±0.36	77±0.65

The metal uptake by the plant in each sample was compared with respect to the organic fertilizer (Table 4.6) and effect of each metal in the plants is described below:

4.2.2.5 Heavy Metals: Barium, Silica, and Arsenic

Barium (Ba)

Barium is an alkaline metal naturally present in soils at relatively high concentrations. According to Clark constants, the amount of Ba present in the Earth ranks 19th among all elements, closely following phosphorus and sulfur (Clark and Washington, 1924). In general, the range of Ba is from 13 to 2050 mg/ kg in the subsoil and from 30 to 1870 mg/ kg in topsoil (Suwa et al., 2008). Barium toxicity for plant and animal has become increasingly important because of its presence in the environment. It finds its way into plants directly by foliage and via water and soil and eventually into animals when they consume barium-enriched plants. The main source of barium in the plant is from the soil (Raghu, 2001).

Barium present in the soil of the study area was off about 0.05% concentration and uptake by the plant as a contaminant. Barium uptake can be reduced up to 90% if, copper tailing and pickling sludge are used as fertilizer. Barium toxicity may be reduced by calcium (Ca), magnesium (Mg), and sulfur (S) supplied through the growth medium, as a result of the antagonistic interaction between these macronutrients and Ba, both in soil and inside the plant (Francisco et al., 2011).

Silica (Si)

Silica is known for not being considered as an essential nutrient for the plant but it is typically abundant in soil and can be taken up by plant roots in greater or lesser quantities. Uptake of silica from soil increases with increasing soil water content. Plants grown in the soils with low soluble silicon levels have greater susceptibility to disease, drought stress and other plant stresses (www.atsdr.cdc.gov/toxprofiles/tp24.pdf). Silica enhances growth and yield, promote upright stature, prevent lodging, promote favorable exposure of leaves to light, provide resistance to bacterial and fungal disease, and provide resistance to low temperature, salinity and influence nitrogen, phosphorous and the composition of other elements in plant tissue (Ma and Takahashi, 2002).

Silica's activity in the soil matrix has been proven to improve micronutrients uptake (boron, copper, iron, manganese, zinc) and reduce toxic metals uptake (Jian, 2004; Williams and Vlamis, 1957; Neumann and Zur Nieden, 2001; Cocker et al., 1998).

Around 73.54% and 1.8% silica is present in copper tailing and pickling sludge respectively. Additionally, 48.5% of silica is present in study area soil. Silica present in copper tailing and pickling sludge enhances the nurturing of the plant growth and prevents it from the heavy and toxic metals.

Arsenic (As)

Arsenic is an element that is nonessential and toxic to plants. Arsenic, when not detoxified, may trigger a sequence of reactions leading to growth inhibition, disruption of photosynthetic and respiratory systems, and stimulation of secondary metabolism (Grag and Singhal, 2011). Presence of Arsenic in soil and copper tailing does not have any considerable effect on plant uptake. This may be due to the presence of lime and iron on pickling sludge and copper tailing (Zheng & Chang, 1998).

4.2.2.6 Macronutrients: Sulfur, Phosphorous, Magnesium, Sodium, and Calcium

Sulfur, Phosphorous, Magnesium, Sodium, and Calcium are the essential macronutrients of the plant. Their presence in pickling sludge and copper tailing does not have any significant effect on plant uptake, although they enhance the growth of plants.

4.2.2.7 Micronutrients: Boron, Chlorine, Copper, Manganese, Iron, Molybdenum, and Zinc

Boron, Chlorine, Copper, Manganese, Iron, Molybdenum, and Zinc are present in a very small amount of waste material and soil. These elements act as micronutrients of the plant. These plant food elements are required in minute quantities, but they are just as important to plant development and profitable crop production as the major nutrients. Iron uptake in leaves of Sample 3 is the highest amongst them due to the presence of high concentration of iron present in pickling sludge, but it has different functions, e.g. promotes the formation of chlorophyll, acts as an oxygen carrier, involves in the reactions cell division and growth (Jones, 1997).

4.2.3 Discussions

Pickling sludge is hazardous in nature, so it cannot be disposed of directly at the disposal sites. Leachate of this sludge may harm both aquatic life and soil. Moreover, disposal of sludge is still a huge problem, as we know that land disposal restrictions are becoming ever increasingly strict, driven by the technical, regulatory and political considerations. The XRF results of pickling sludge and copper tailing showed that they consist of micro and macronutrients for plants. Hence, an attempt has been made to investigate the feasibility of utilizing the industrial waste as fertilizer for the ornamental plant. The oleander plant (ornamental plant) was planted in four pots by keeping the ratio of soil to sludge in 3:1. The possibility of reuse of copper tailings and pickling sludge as fertilizers was verified through the experiment. It was found that these industrial wastes have the potential to be used as fertilizing agents in ornamental plants. The sample containing copper tailings and pickling waste has the most profound effect. Pickling sludge, when used alone, hindered the growth of the plant may be due to the high concentration of lime, but when used along with copper tailings produced positive results. Hence, copper tailings used along with the sludge produced from spent pickling liquor could be used as a fertilizing agent for the ornamental plant. The XRF results of plants leaves show that the heavy metals present in pickling sludge and copper tailing do not have any deprived effect on plant growth and its metals uptake. Moreover, pickling sludge along with copper tailing as fertilizer reduces the uptake of barium contaminant because calcium (Ca), magnesium (Mg), and sulfur (S) supplied through the growth medium, as a result of the antagonistic interaction between these macronutrients and Ba, both in soil and inside the plant (Francisco et al., 2011).

4.3 Investigations on the Feasibility of Utilizing Sludge in Interlocking Tiles

In the previous section, an effort was made to utilize pickling sludge as fertilizer. In this section, an attempt has been made to investigate the feasibility of utilizing the pickling sludge in interlocking tiles by partially replacing the cement with pickling sludge.

4.3.1 Materials and procedure

Pickling liquor was treated with lime (commercial grade) as described in previous section 3.3 and the pickling sludge produced in as described in section 3.3.1 was dried in the oven (Figure 4.2) and used for the study.

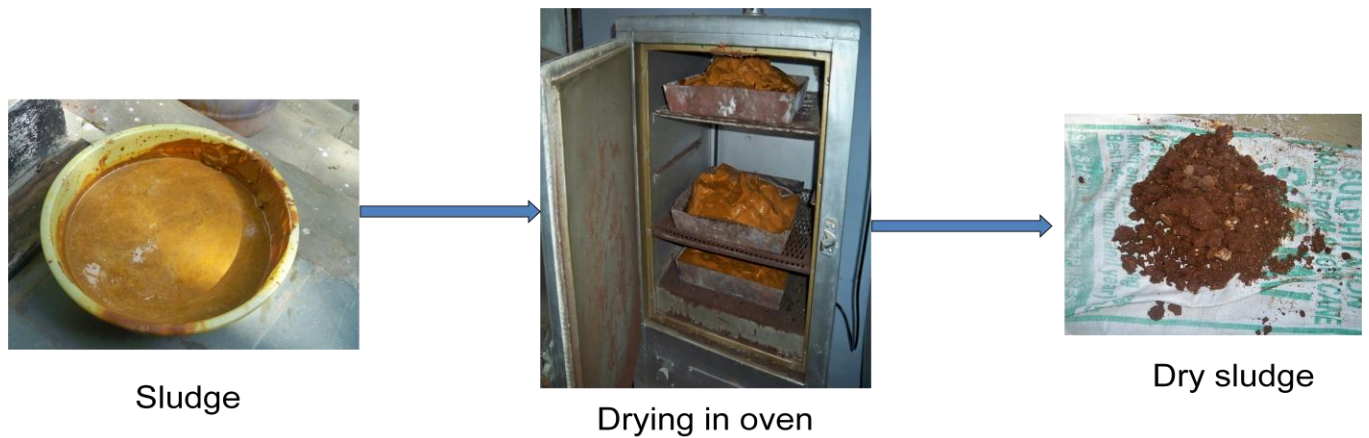
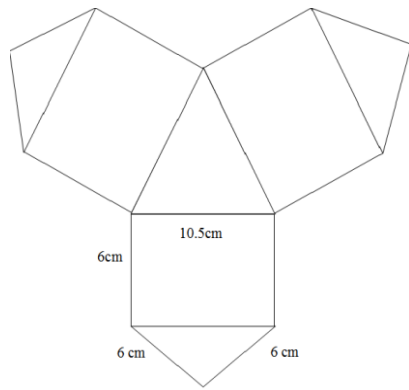


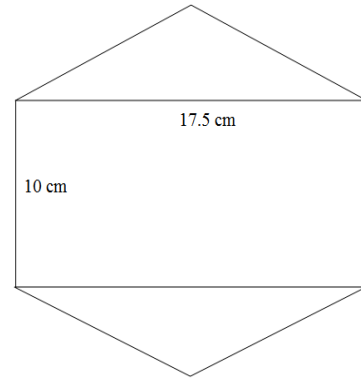
Figure 4.2: Sequence of dry sludge produced from wet sludge

4.3.1.1 Preparation, casting, and curing of specimens

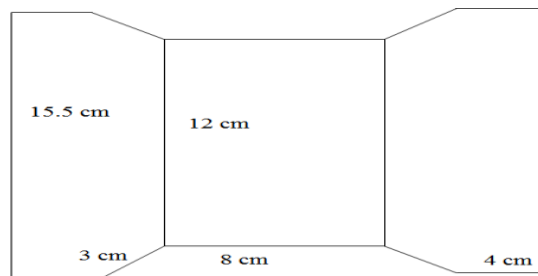
Three different shapes of tiles (Dumbbell, hexagonal and triangular shapes (Figure 4.3)) were prepared that can be used as footpath tiles and safely immobilize the heavy metals present in the sludge. Table 4.7 presents the composition of these tiles. The specimens were prepared by adding different proportions of sludge as a substitute to cement with cement to sand to stone grit in the ratio 1:2:4.



Triangular



Hexagonal



Dumbbell

Figure 4.3: Different shapes of tiles

Table 4.7: Designation of tiles

Tiles Code	Thickness (in mm)	% of Sludge (As a partial replacement of sludge)	Shapes
A (Blank)	80	-	Dumbbell (D)
A	80	2.5	Dumbbell (D)
B (Blank)	60	-	Dumbbell (D), Hexagonal (H), Triangular (T)
C	60	2.5	Dumbbell (D), Hexagonal (H), Triangular (T)
D	60	5	Dumbbell (D), Hexagonal (H), Triangular (T)
E	60	7.5	Dumbbell (D), Hexagonal (H), Triangular (T)
F	60	10	Dumbbell (D), Hexagonal (H), Triangular (T)

4.3.2 Cement

In the study, ordinary Portland cement 43 grade was used.

4.3.2.1 *Chemical properties of cement*

Chemical properties of the cement were determined as per IS (4032, 1985).

(a) Silica

A sample of 0.5 g was taken in an evaporating dish. It was moistened with 10 ml of distilled water at room temperature to prevent lumping, and 5 to 10 ml of hydrochloric acid was added. It was digested with the aid of gentle heat and agitation until the sample was completely dissolved. Dissolution may be aided by light pressure with the flattened end of a glass rod. The solution was evaporated to dryness on a steam-bath. Without heating the residue, it was treated with 5 to 10 ml of hydrochloric acid and then with an equal amount of water. Then dish was covered and contents were digested for 10 minutes on the water-bath. The solution was diluted with an equal volume of hot water, the sample was filtered immediately through an ashless filter paper (Whatman No. 40 or its equivalent), and separated silica (SiO_2) was washed thoroughly with hot water and residue is reserved.

The filtrate was again evaporated to dryness, baking the residue in an oven for one hour at 105 to 110°C. Then the residue was treated with 10 to 15 ml of hydrochloric acid (1: 1) and the solution was heated on water-bath. The solution was diluted with an equal volume of hot water catch and the small amount of silica was washed with help of another filter paper. Filtrate and washings were reserved for the determination of combined alumina and ferric oxide.

Papers containing the residues were transferred to a weighed platinum crucible. The papers were dried and ignited, first at a low heat until the carbon of the filter paper was completely consumed without inflaming, and finally at 1100 to 1200°C until the weight remains constant.

Ignited residues obtained were treated, which contain a small amount of impurities, with 1 to 2 ml of distilled water, about 10 ml of hydrofluoric acid and 2 drops of sulphuric acid and

evaporated cautiously to dryness. Finally, the small residue was heated at 1050 to 1100°C for a minute or two; cooled and weighed. The difference between this weight and the weight of ignited sample represents the amounts of silica:

$$\text{Silica (\%)} = 200 (W_1 - W_2) \quad (4.1)$$

Where, W_1 = weight of silica + (insoluble impurities – residue), and W_2 = weight of impurities

To this amount of silica, the amount of silica recovered from the residue derived from the combined precipitates of alumina and ferric oxide was added.

A 0.5 g of sodium or potassium persulphate was added to the crucible and heated until the small residue of impurities was dissolved in the melt. Fused mass in cooled and dissolved in water, and added to the filtrate and washings were reserved for the determinations of the combined alumina and ferric oxide.

(b) Ferric Oxide

The filtrate was prepared with a procedure as given in (a) above. Filtrates were mixed to and make up the volume in a 250-ml volumetric flask. 25 ml of solution was taken reserved from the above 250 ml volumetric flask and diluted with ammonium hydroxide (1: 6) till turbidity appears. The turbidity was cleared with a minimum amount of dilute hydrochloric acid (1: 10) and a few drops are added in excess to adjust the pH to approximately 1 to 1.5 and it was shaken well. Then 100 mg of sulphosalicylic acid was added and titrated with 0.01 M EDTA solution carefully to a colorless or pale yellow solution. The percentage of Fe_2O_3 was calculated as below:

1 ml of 0.01 M EDTA = 0.7985 mg of Fe_2O_3

$$\text{Iron oxide (Fe}_2\text{O}_3\text{) \%} = \frac{0.7985 \times V}{W} \quad (4.2)$$

Where, V = Volume of EDTA used in ml, and W = Weight of the sample in g.

(c) Alumina

A 25 ml of solution was taken reserved under (b) and titrated for iron at pH approximately 1 to 1.5 with EDTA using sulphosalicylic acid as an indicator as given in (b). 15 ml standard EDTA solution was added. Then, 1 ml of phosphoric acid (1 : 3), 5 ml of sulphuric acid (1 : 3) and one drop of thymol blue were added to the titration flask. The ammonium acetate solution was added by stirring until the color changes from red to yellow. 25 ml of ammonium acetate was added in excess to obtain pH approximately 6. The solution was heated to boiling for one minute and then cooled. 50 mg of solid xylenol orange indicator and bismuth nitrate solution were added slowly with stirring until the color of the solution changes from yellow to red. Bismuth nitrate solution in excess was added. The solution was titrated with 0.01 M EDTA to a sharp yellow endpoint red color. The percentage of Al_2O_3 was calculated as below:

$$V = V_1 - V_2 - (V_3 \times E) \quad (4.3)$$

Where, V = Volume of EDTA for alumina in ml, V_1 = Total volume of EDTA used in the titration in ml, V_2 = Volume of EDTA used for iron in ml, V_3 = Total volume of bismuth nitrate solution used in the titration in ml, E = Equivalence of 1 ml of bismuth nitrate solution

1 ml of 0.01 M EDTA \equiv 0.5098 mg of Al_2O_3

$$\text{Aluminium oxide (Al}_2\text{O}_3) (\%) = \frac{0.5098 \times V}{W} \quad (4.4)$$

Where W = Weight of the sample in g.

(d) Calcium Oxide

10 ml of solution reserved under (b) was taken in a 250 ml conical flask. 5 ml of 1 : 1 glycerol and 5 ml of diethylamine were added with constant stirring. 10 ml of 4N sodium hydroxide solution was added and shaken well to adjust pH to a highly alkaline range of 12 or slightly more. Approximately 50 ml of distilled water and 50 mg of solid Patton-Reeder's indicators were added. The solution was titrated against 0.01 M EDTA solution to a sharp change in color from wine red to clear blue. The percentage of CaO was calculated as below:

1 ml of 0.01 M EDTA \equiv 0.5608 mg of CaO

$$\text{Calcium Oxide (CaO) (\%)} = \frac{0.05608 \times 25 \times V}{W} \quad (4.5)$$

Where V = Volume of EDTA used in ml and W = Weight of the sample in g.

(e) Magnesium Oxide

10 ml of solution reserved under (b) was taken. 5 ml of 1: 1 triethanolamine with constant shaking and 20 ml of buffer solution pH 10 were added. 50 mg of solid thymol phthalaxone indicator followed by approximately 50 ml of distilled water was added. The solution was titrated against standard 0.01 M EDTA solution until the color changes from blue to clear pink. This titration gives the sum of calcium and magnesium oxide present in the solution. Titre value of magnesium oxide was obtained by subtracting the titre value of calcium oxide from the total titre value. The percentage of MgO was calculated as given below:

1 ml of 0.01 M EDTA \equiv 0.4032 mg of MgO

$$\text{Magnesium oxide (MgO) \%} = \frac{0.04032 \times 25 \times (V_1 - V)}{W} \quad (4.6)$$

Where, V_1 = Volume of EDTA used in this titration in ml, V = Volume of EDTA used in CaO determination in ml, and W = Weight of the sample in g.

(f) Sulphuric Anhydride

To 1 g of sample, 25 ml of cold water and 5 ml of hydrochloric acid was added and the mixture was stirred vigorously. The solution was heated and material was ground with the flattened end of a glass rod until it was evident that the decomposition of the cement was complete. The solution was diluted to 50 ml and digested for 15 minutes at a temperature just below boiling. The residue was filtered and washed thoroughly with hot water. The filter paper with the residue was set aside. The filtrate was diluted to 250 ml and heated to boiling. 10 ml of hot barium chloride (100 g/l) solution was added slowly drop by drop and continued the boiling until the precipitate was well formed. The solution was digested on a steam-bath for 4 hours. The precipitate was filtered through a Whatman No. 42 filter paper or equivalent and the precipitate was washed thoroughly. Filter paper and the contents in a weighed

porcelain crucible were slowly incinerated without inflaming. It was then ignited at 800 to 900°C, cooled in a desiccator and weighed the barium sulfate. The sulphuric anhydride content of the material taken for the test was calculated. The percentage of SO₃ was calculated as follows:

$$\text{SO}_3 \% = W \times 34.3 \quad (4.7)$$

Where, W = weight of residue (BaSO₄) in g and 34.3 = molecular ratio of SO₃ to BaSO₄ (0.343), multiplied by 100.

(g) Sodium Oxide and Potassium Oxide

1.000 ± 0.001 g of cement sample was placed in a 150-ml beaker and dispersed with 20 ml of water using a swirling motion of the beaker. While still swirling, 5.0 ml of hydrochloric acid was added all at once. It was diluted immediately to 50 ml with water. The lumps of cement remaining undispersed were broken with a flat-end stirring rod. It was digested on the steam-bath for 15 minutes, and then filtered through a medium texture filter paper into a 100-ml volumetric flask. Beaker and paper were washed thoroughly with hot water, the content of the flask was cooled to room temperature. It was diluted to 100 ml, and the solution was mixed thoroughly.

(i) *Procedure for determination of sodium oxide* – the flame photometer was warmed up and adjusted for the determination of sodium oxide. Immediately following the adjustment and without changing any instrumental setting, the cement solution was atomized and the scale reading was noted. The standard solution was selected which immediately bracket the cement solution in sodium oxide content and their readings were observed. Their values agreed within one division on the scale with the values previously established during calibration of the apparatus. Finally, an alternate unknown solution was used until readings for the unknown agree within one division on the transmission scale and readings for the standards similarly agree with the calibration points. Average of the last two readings obtained was recorded as the value of the unknown solution.

(ii) *Procedure for determination of potassium oxide* — the procedure described was repeated in above para except that the instrument was adjusted for the determination of potassium oxide.

(iii) *Calculations for Na₂O and K₂O* — from the recorded averages of meter readings for potassium oxide and sodium oxide in the unknown sample, the percentage of each oxide from its respective calibration curve was read.

(iv) *Loss on Ignition*

1.00 g of sample was heated for 15 minutes in a weighed and covered porcelain crucible of 20 to 25 ml capacity by placing it in a muffle furnace at a temperature between 900° and 1000°C; it was cooled and weighed. The loss in weight was checked by a second heating for 5 minutes and re-weighing. The loss in weight was recorded as the loss on ignition, was calculated as below:

$$\text{Percent loss on ignition} = \text{loss in weight} \times 100 \quad (4.8)$$

4.3.2.2 Physical properties of the cement

Physical properties of the cement were analyzed in the laboratory. Following tests were carried out for the analysis:

(a) *Consistency of standard cement paste as per the IS: (4031 Part 4, 1988)*

The standard consistency of a cement paste is defined as that consistency which will permit the Vicat Plunger G (IS 5513-1996) to penetrate to a point 5 to 7 mm from the bottom of the Vicat mould. The cement paste was tested as described below.

A paste of weighed quantity of cement with a weighed quantity of potable water was prepared; taking care that the time of gauging was not less than 3 minutes, not more than 5 min. The gauging was completed before any sign of setting occurs. The gauging time was counted from the time of adding water to the dry cement until commencing to fill the mould. Vicat mould E was filled with this paste with the mould resting on a non-porous plate. After completely filling the mould, the surface of the paste was smoothed by making it level with the top of the mould. The mould was slightly shaken to expel the air. Clean appliances were used for filling the mould.

The test block was placed in the mould, together with the non-porous resting plate, under the rod bearing the plunger. The plunger was lowered gently to touch the surface of the test block, and it was quickly released, allowing it to sink into the paste. This operation was carried out immediately after filling the mould. Trial pastes were prepared with varying percentages of water and test as described above until the amount of water necessary for making up the standard consistency as defined in the first para of (A). The amount of water was expressed as a percentage by mass of the dry cement to the first place of decimal.

(b) Soundness of cement as per IS: (4031 Part 3, 1988)

The lightly oiled mould was placed on a lightly oiled glass sheet, and it was filled with cement paste formed by gauging cement with 0.78 times the water required to give a paste of standard consistency. The paste was gauged in the manner and under the conditions prescribed in IS 4031 (Part 4), 1988, taking care to keep the edges of the mould gently together. The mould was covered with another piece of the lightly oiled glass sheet and a small weight was placed on this covering glass sheet. The whole assembly was immediately submerged in water at a temperature of $27 \pm 2^\circ\text{C}$, and was kept there for 24 hours.

The distance separating the indicator points to the nearest 0.5 mm was measured. The mould was again submerged in water at the temperature prescribed above. The water was brought to boiling, with the mould kept submerged for 25 to 30 minutes, and was kept boiling for three hours. The mould was removed from the water and is allowed to cool. The distance was measured between the indicator points. The difference between these two measurements indicates the expansion of the cement.

Mean of two values to the nearest 0.5 mm to represent the expansion of cement was calculated.

(c) Initial and final setting time of cement as per IS: (4031 Part 5, 1988)

A neat cement paste was prepared by gauging the cement with 0.85 times the water required to give a paste of standard consistency. Potable water was used in preparing the paste. The paste was gauged in the manner and under the conditions prescribed in IS: 4031 (Part 4)-1988. Stop-watch was started at the instant when water was added to the cement. Vicat mould E was filled with the gauged cement paste with the mould was resting on a nonporous plate. Mould was filled completely and the surface of the paste was smoothed off making it level with the top of the mould. The cement block thus prepared in the mould was the test block.

(i) Determination of initial setting time

Test block was placed confined in mould and resting on the non-porous plate, under the rod bearing the needle (C). The needle was gently lowered until it comes in contact with the surface of the test block and was quickly released, allowing it to penetrate into the test block. In the beginning, the needle completely pierced the test block. This procedure was repeated until the needle when brought in contact with the test block and released as described above, fails to pierce the block beyond 5.0 ± 0.5 mm measured from the bottom of the mould. The period elapsing between the time when water was added to the cement and the time at which the needle fails to pierce the test block to a point 5.0 ± 0.5 mm measured from the bottom of the mould was the initial setting time.

(ii) Determination of final setting time

The needle (C) of the Vicat apparatus was replaced by the needle with an annular attachment (F). The cement was considered as finally set when, upon applying the needle gently to the surface of the test block, the needle makes an impression thereon, while the attachment fails to do so. The period elapsing between the time when water was added to the cement and the time at which the needle makes an impression on the surface of test block while the attachment fails to do so was the final setting time.

4.3.2.3 Fine aggregate (Sand)

Fine aggregate was analyzed as per IS: 383-1970. The sample was brought to an air-dry condition before weighing and sieving. This was achieved by heating at a temperature of 100 to 1100 °C. The air-dry sample was weighed and sieved successively on the appropriate sieves starting with the largest. Care was taken to ensure that the sieves were clean before use.

Each sieve is shaken separately over a clean tray until not more than a trace passes, for a period of not less than two minutes. The shaking is done with a varied motion, backward and forward, left to right, circular clockwise and anti-clockwise, and with frequent jarring, so that the material was kept moving over the sieve surface infrequently changing directions. The material was not forced through the sieve by hand pressure, but on sieves coarser than 20 mm, placing of particles was permitted. Lumps of fine material were broken by gentle pressure with fingers against the side of the sieve. A light brushing with a soft brush on the underside of the sieve was used to clear the sieve openings.

A light brushing with a fine camel hair brush may be used on the 150 μ and 75 μ IS sieves to prevent aggregation of powder and blinding of apertures. (Stiff or worn out brushes shall not be used for this purpose and pressure was not applied to the surface of the sieve to force particles through the mesh). On completion of sieving, the material retained on each sieve together with any material cleaned from the mesh was weighed.

In order to prevent binding of the sieve apertures by overloading, the amount of aggregate placed on each sieve was such that the weight of the aggregate retained on the sieve at the completion of the operation was not greater than the value given for that sieve in Table 4.8. Minimum weights of the sample to be taken for sieving are given in Table 4.9.

Table 4.8: Maximum weight to be retained at the completion of sieving (clause 2.4.4) IS: 2386 (Part I) – 1963

Coarse Aggregate			Fine Aggregate	
IS Sieve Designation (mm)	Maximum weight for		IS Sieve	Maximum weight for 20-cm dia sieve (g)
	45-cm dia sieve (kg)	30-cm dia sieve (kg)		
50	10	4.5	2.36-mm	200
40	8	3.5	1.18-mm	100
31.5 or 25	6	2.5	-	-
20	4	2.0	600-micron	75
16 or 12.5	3	1.5	300-micron	50
10	2	1.0	-	-
6.3	1.5	0.75	150-micron	40
4.75	1.0	0.50	75-micron	25
3.35	--	0.30	-	-

Table 4.9: Minimum weight of sample for sieve analysis (clauses 2.4.4, 2.5 and 2.5.2) IS: 2386 (Part I) – 1963

Maximum size present in substantial proportions (mm)	Minimum weight of sample to be taken for sieving (kg)
63	50
50	35
40 or 31.5	15
5	5
20 or 16	2
12.5	1
10	0.5
6.3	0.2
4.75	0.2
2.36	0.1

Fine aggregates were specified as per Table 4.10 of IS: (383, 1970).

Table 4.10: Grading of fine aggregates (clause 4.3) IS : 383 – 1970

IS Sieve Designation	Percentage Passing for			
	Grading Zone I	Grading Zone II	Grading Zone III	Grading Zone IV
10 mm	100	100	100	100
4.75 mm	90-100	90-100	90-100	95-100
2.36 mm	60-95	90-100	90-100	95-100
1.18 mm	30-70	55-90	75-100	90-100
600 micron	15-34	35-59	60-79	80-100
300 micron	5-20	8-30	12-40	15-50
150 micron	0-10	0-10	0-10	0-15

Note 1 - For crushed stone sands, the permissible limit on 150 μ IS sieve is increased to 20%. This does not affect 5% allowance permitted in clause 4.3 applying to other sieve sizes.

Note 2 - Fine aggregate complying with the requirements of any grading zone in table 3.3 for concrete but the actual quality of concrete produced will depend upon a number of factors including proportions.

Note 3 - Where concrete of high strength and good durability is required, fine aggregate conforming to any one of the four grading zones may be used, but the concrete mix should be properly designed. As the sieve size is progressively finer, from grading zones I to IV, the ratio of fine aggregate to coarse aggregate should be progressively reduced. The most suitable fine to coarse ratio to be used for any particular mix will, however, depend upon the actual grading, particle shape and surface texture of both fine and coarse aggregates.

Note 4 - It is recommended that fine aggregate conforming to grading zone IV may not be used in reinforced concrete unless tests are made to ascertain the suitability of proposed mix proportions.

4.3.2.4 Coarse aggregate

Coarse aggregate was used as per IS: (383, 1970). Coarse aggregates were specified as per Table 4.11 of IS: 383 – 1970.

Table 4.11: Coarse aggregate specifications (clauses 4.1 & 4.2) IS: 383 - 1970

IS Sieve Designation (mm)	Percentage Passing for Single-Sized Aggregate of Nominal Size						Percentage Passing for Graded Aggregate for Nominal Size			
	63 mm	40 mm	20 mm	16 mm	12.5 mm	10 mm	40 mm	20 mm	16 mm	12.5 mm
80	100	-	-	-	-	-	100	-	-	-
63	85 to 100	100	-	-	-	-	-	-	-	-
40	0 to 30	85 to 100	100	-	-	-	95 to 100	100	-	-
20	0 to 5	0 to 20	85 to 100	100	-	-	30 to 70	95 to 100	100	100
16	-	-	-	85 to 100	100	-	-	-	90 to 100	-
12.5	-	-	-	-	85 to 100	100	-	-	-	90 to 100
10	0 to 5	0 to 5	0 to 20	0 to 30	0 to 45	85 to 100	10 to 35	25 to 55	30 to 70	40 to 85
4.75	-	-	0 to 5	0 to 5	0 to 10	0 to 20	0 to 5	0 to 10	0 to 10	0 to 10
2.36	-	-	-	-	-	0 to 5	-	-	-	-

4.3.2.5 Casting of tiles

All the concrete was mixed in Hand Feed Concrete Mixer (Figure 4.4). The speed of the mixer was about 25 rpm. All cement-sludge concrete cubes were cast in cast iron mould at 27 ± 2 °C. For compaction of concrete cubes vibrating Table was used (Figure 4.5). The Vibrating Table was operated by 5 HP motor with speed of 12000 ± 400 rpm. All the concrete cubes (Figure 4.6) were cured with moist gunny bags and after 24 hours all the cubes were dipped in water at the temperature of 27 ± 2 °C.



Figure 4.4: Hand feed concrete mixer used in the study



Figure 4.5: Casting of Tiles



Figure 4.6: Tiles used in the study

4.3.2.6 Physical and chemical properties of tiles

The physical analysis of pavement tiles was performed as per IS: 15658, 2006.

4.3.2.6.1 Block Density

Three blocks taken at random from the samples were dried to constant mass in a suitable oven heated to approximately 100 °C. After cooling the blocks to room temperature, the dimensions of each block were measured and the overall volume computed. The blocks were then weighed and the density of each block was calculated. The average for the three blocks was taken as the mean density.

4.3.2.6.2 Absorption

The test specimens were completely engulfed in water at room temperature for 24 hours. The specimens were then weighed, while suspended by a metal wire and completely submerged in water. They were removed from the water and allowed to drain for one minute of placing them on a 10 mm wire mesh, visible surface water being removed with a damp cloth. Subsequent to saturation, all specimens were dried in a ventilated oven at 100°C for 24 hours and immediately weighed.

4.3.2.6.3 Drying shrinkage

The specimens used for the drying shrinkage test were immersed in water for 4 days, the temperature is maintained at 27 ± 2 °C for at least 4 hours prior to the removal of the specimens and the wet length measured. The moisture movement was determined as the difference between the dry and wet lengths and expressed as a percentage of the dry length for each specimen.

4.3.2.6.4 TCLP test

TCLP test (18 hrs) was conducted on the tiles containing pickling sludge as per US EPA standard. After 28 days of curing, a slice of concrete approximately 9.5 mm thick was cut from the mid-height of the tile. A part of each slice weighing approximately 100 g was crushed carefully using a hammer so that all particles were 9.5 mm, but the variation of the

particle size distribution was not significant. Each crushed concrete sample was treated with an acetic acid solution of pH 2.8 at a liquid-to-solid ratio of 20:1 for a period of 18 h in the bottles. The bottles were shaken at 28–30 rpm in an Orbital shaker (Figure 4.7) at room temperature for 18 h. At the end of the extraction, the leachates were filtered through a 0.45 mm membrane filter to remove suspended solids. The pH of the filtrate was measured and the leachate was analyzed on UV Spectrophotometer for pH and iron.



Figure 4.7: Orbital shaker for TCLP test

4.3.2.7 Compressive strength

The compressive strength of all the cement-sludge sand mortar cubes was tested by using a Compression Testing Machine (SCHAFF HOUSE, Switzerland and supplied by Alfred J. Amsler & Co., Figure 4.8). Working range of the Compression Testing Machine was 0-200 tones.



Figure 4.8: Compressive strength test of the tiles

4.3.3 Results and Discussions

4.3.3.1 Characterization of the pickling sludge

The pickling sludge characterization results are presented in Table 4.12. The pH of pickling sludge is 7.5

Table 4.12: Pickling sludge characterization

Parameters	Concentration (%)
Lime (CaO)	71.52%
Oxygen (O)	26.32%
Chloride (Cl)	12.45%
Magnesia (MgO)	6.19%
Iron Oxide (Fe ₂ O ₃)	26.12%
Silica (SiO ₂)	1.87%
Alumina (Al ₂ O ₃)	0.4%
Loss on Ignition (LOI) at the temperature of 1050 °C	11.53%
Bulk Density	2020 kg/m ³
Moisture content of the sludge	1.5%

4.3.3.2 Sieve analysis of sludge

Oven dried sludge samples of 500 g each had been taken for sieve analysis. Sieve analysis was carried out by using the standard procedure. Sieve analysis results are shown in Table 4.13.

Table 4.13 shows that more than 50% of all the sludge has a particle size greater than 178 µm and below 35 µm size these are negligible. The particle size distribution graph of pickling sludge is given in Annexure H.

Table 4.13: Sieve analysis of pickling sludge

Sieve size (μm)	Pickling Sludge (% retained)
180	51.1
150	4.8
125	8.9
105	3.9
90	6.2
75	7.8
63	8.3
53	3.2
35	5.8

4.3.3.3 Chemical Composition and Physical Properties of the Cement

Ordinary Portland cement 43 grade was used for the study. Chemical and physical properties of the cement are presented in Table 4.14.

4.3.3.4 Fine Aggregate (Sand) Analysis

Sieve analysis of the fine aggregate is presented in Table 4.15.

Table 4.14: Chemical and physical properties of cement

Chemical Analysis		
S. No.	Parameter	Value
1	Lime (CaO)	63.5%
2	Silica (SiO ₂)	19.05 %
3	Alumina (Al ₂ O ₃)	4.2%
4	Iron Oxide (Fe ₂ O ₃)	3.1%
5	Magnesia (MgO)	2.9 %
6	Sulphur Tri Oxide (SO ₃)	2.5%
7	Soda and/or Potash (Na ₂ O + K ₂ O)	0.9%
8	Loss on Ignition	2.1%
Physical Tests		
1	Consistency of standard cement paste	28%
2	Soundness of cement	3.5 mm
3	Initial setting time of cement	125 min
4	Final setting time of cement	182 min
5	Fineness by air permeability	2698 cm ² /g

Table 4.15: Sieve analysis results of fine aggregate

IS Sieve Size	% Retained	Remark
4.75 mm	10.73	Conforming to grading zone (3) of Table 4.9 of IS: 383-1970
2.36 mm	21.03	
1.7 mm	30.69	
1.18 mm	40.34	
600 µm	51.64	
300 µm	64.36	
150 µm	79.33	
90 µm	90.54	
Remaining	100	

4.3.3.5 Coarse Aggregate

Sieve analysis of coarse aggregate used in the study is shown in Table 4.16.

Table 4.16: Sieve analysis results of coarse aggregate

IS Sieve Size	Coarse Aggregate (Percent Passing)	Remarks
20 mm	100	Special type of coarse aggregate is used for the production of cement concrete pavement tiles. Commercial name of the gravel is zero size
10 mm	100	

4.3.3.6 TCLP test for pavement tiles

Table 4.17 shows the Fe leachate concentration of pickling sludge and pavement tiles at 28 days curing. It is clear from the results that Fe concentration is negligible in leachate. It is due to non-dissolving nature of pickling sludge in acids and S/S (Singhal et al., 2008).

Table 4.17: TCLP (18h) test results for sludge-concrete mix pavement tiles after 28 days of curing

Tiles Code	Thickness (mm)	% of Sludge (As a partial replacement of sludge)	Iron (mg/l)	pH
B (Blank)	60	-	BDL	5.1
C	60	2.5	BDL	5.2
D	60	5	BDL	5.1
E	60	7.5	BDL	5
F	60	10	BDL	5

*Note: BDL-Below detectable limit
Average of three samples*

4.3.3.7 Block Density

The Block Density of the various samples was calculated by measuring weights of the blocks in mainly three shapes namely Hexagonal, Triangular and Dumbbell with volumes of 1688.745 cc, 1823.8 cc and 1735.2 cc. The density was found to be in the range of 2.24 – 2.4 g/cc (Table 4.18). Although the densities were found to be fairly close to each other for all the three shapes of tiles used in the experiments, the Hexagonal ones were found to have the greatest density of all due to their compact size. Moreover, it was observed that the addition of sludge to the tiles didn't vary the block density and there was a marginal increase moving from B to F.

Table 4.18: Block Density of sludge-concrete mix pavement tiles

Sample	B			C			D			E			F		
	H	T	D	H	T	D	H	T	D	H	T	D	H	T	D
Weight (kg)	3.89	4.08	3.82	3.94	4.23	3.92	3.91	4.03	3.87	4.12	4.24	4.06	3.76	4.05	3.82
Density (gm/cc)	2.30	2.23	2.20	2.33	2.31	2.25	2.31	2.20	2.23	2.43	2.32	2.33	2.22	2.22	2.20

Note: Average of three samples

4.3.3.8 Absorption

Table 4.19: Absorption of sludge-concrete mix pavement tiles (Average of three samples)

Sample	B			C			D			E			F		
	H	T	D	H	T	D	H	T	D	H	T	D	H	T	D
Wet weight (kg)	3.94	4.15	3.88	4.01	4.33	4.12	3.97	4.12	3.84	4.19	4.30	4.13	3.81	4.13	3.92
Dry weight (kg)	3.70	3.96	3.65	3.79	4.15	3.87	3.84	3.96	3.65	3.98	4.05	3.90	3.71	3.91	3.71
Absorption %	5.99	4.67	5.90	5.44	4.11	6.04	3.22	4.00	5.00	5.04	5.91	5.47	2.62	5.38	5.36

Note: Average of three samples

The tests for calculating the absorption of water showed promising results with the difference in dry and wet weights not varying more than 6% in any of the specimens. This displays the ability of the tiles to withstand wet conditions and maintain agreeable compressive strength owing to low absorption of water. It is safe to assume that 7.5% is the optimum sludge concentration in order to obtain least water absorption as all three specimens gave the best results as shown in Table 4.19.

4.3.3.9 Drying Shrinkage

The dry and wet lengths of the sample were not found to vary by more than 1%. It is safe to conclude that there was not much deformation and decrease in strength even when the samples were in contact with water for longer durations. However, it increased for the Dumbbell shaped pavement tiles with an increase in the sludge concentration. Hexagonal tiles were not affected by the amount of addition of sludge and a constant value of 0.116% was observed in all three cases, i.e. 2.5%, 5% and 7.5% (Table 4.20).

Table 4.20: Drying Shrinkage of sludge-concrete mix pavement tiles

Sample	B			C			D			E			F		
	H	T	D	H	T	D	H	T	D	H	T	D	H	T	D
Dry length (cm)	17.19	18.17	20.16	17.19	18.19	20.12	17.19	18.18	20.12	17.17	18.18	20.17	17.05	18.19	20.13
Wet length (cm)	17.2	18.19	20.17	17.21	18.2	20.13	17.21	18.19	20.14	17.19	18.2	20.19	17.08	18.21	20.15
Drying shrinkage (%)	0.058	0.110	0.050	0.116	0.055	0.055	0.116	0.055	0.099	0.116	0.110	0.099	0.176	0.110	0.099

Note: Average of three samples

4.3.3.10 Compressive Strength

The compressive strength at 7 and 28 days is given in Table 4.21 and Table 4.22 respectively is average of 5 samples.

The results of compressive strength at 7 and 28 days following the same trend in the samples with the Dumbbell shaped specimen displaying maximum strength and the Hexagonal ones the minimum. Compact, symmetrical shape with the lesser surface area could have been one of the vital aspects attributing to the high compressive strength of the Dumbbell shaped tiles. A change in the thickness of the tiles from 60 mm to 80 mm helped in improving strength characteristics.

Table 4.21: Compressive Strength of sludge-concrete mix pavement tiles after 7 days

Tiles Code	Thickness (mm)	% of Sludge (As a partial replacement of sludge)	Compressive Strength After 7days		
			Dumbbell (N/mm ²)	Hexagonal (N/mm ²)	Triangular (N/mm ²)
A (Blank)	80	-	25.93	-	-
A	80	2.5	30.25	-	-
B (Blank)	60	-	23.22	20.32	21.17
C	60	2	26.06	22.66	23.56
D	60	5	29.93	24.48	27.12
E	60	7.5	34.66	26.42	32.16
F	60	10	40.12	30.42	39.19

Note: Average of five samples

Table 4.22: Compressive Strength of sludge-concrete mix pavement tiles after 28 days

Tiles Code	Thickness (mm)	% of Sludge (As a partial replacement of sludge)	Compressive Strength After 28 days		
			Dumbbell (N/mm ²)	Hexagonal (N/mm ²)	Triangular (N/mm ²)
A (Blank)	80	-	30.25	-	-
A	80	2.5	35.63	-	-
B (Blank)	60	-	28.8	23.781	25.03
C	60	2	31.49	29.30	30.27
D	60	5	35.27	30.47	34.41
E	60	7.5	41.09	32.21	38.89
F	60	10	50.03	37.23	47.58

Note: Average of five samples

The promising outcome of the experiments was the fact that an increase in the sludge content was directly proportional to the strength of the specimens. On varying the sludge concentration from 0 to 10%, the compressive strength was found to increase irrespective of the thickness or the shape of the tile. Replacing some of the Portland cement with pickling sludge ignites a pozzolanic reaction within the hydrated paste that, via a molecular-level reclamation process and converts into additional Calcium Silica Hydrate (CSH) gel in the sludge cement concrete mix. Moreover, this CSH may facilitate the cementation process and contribute to the strength of the tiles (Sabir et al., 2001). This is also confirmed by the XRD analysis of the tiles. The XRD analysis of samples B, D and F has been carried out (Figures 4.9 to 4.11). The XRD analysis of the tiles revealed that gypsum, dicalcium silicate, tricalcium silicate and C-S-H gel components present in the sludge-concrete mix are responsible for gaining the compressive strength of the tiles.

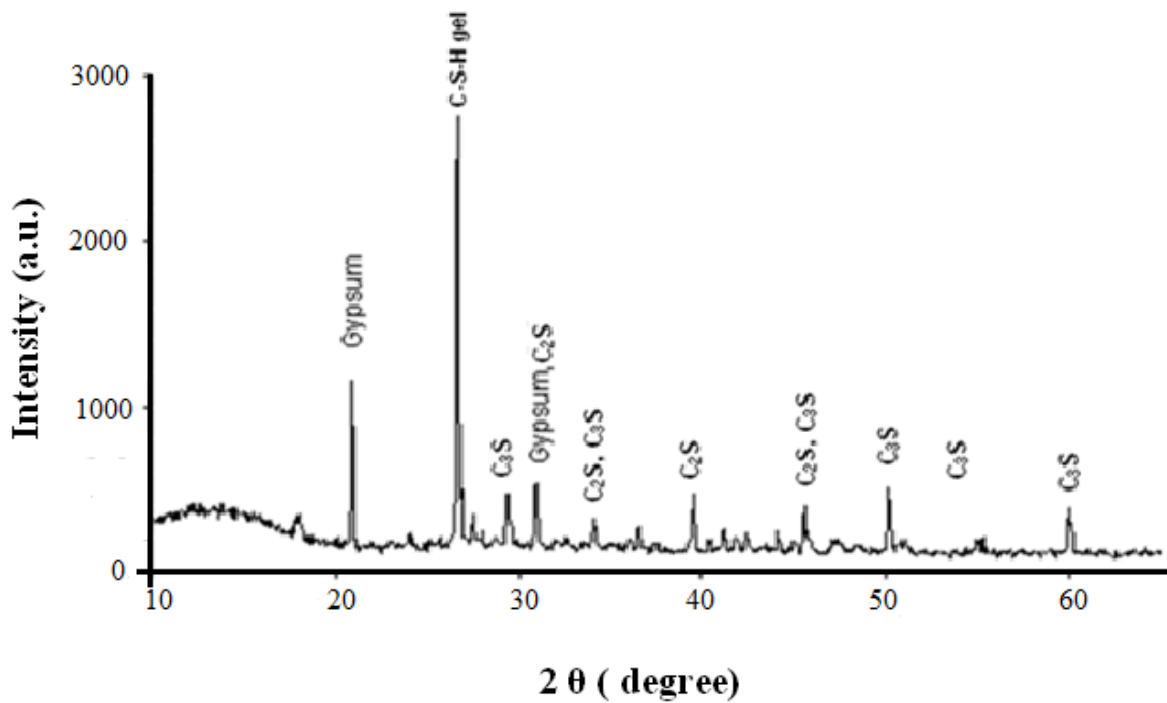


Figure 4.9: XRD spectrum of B tile sample

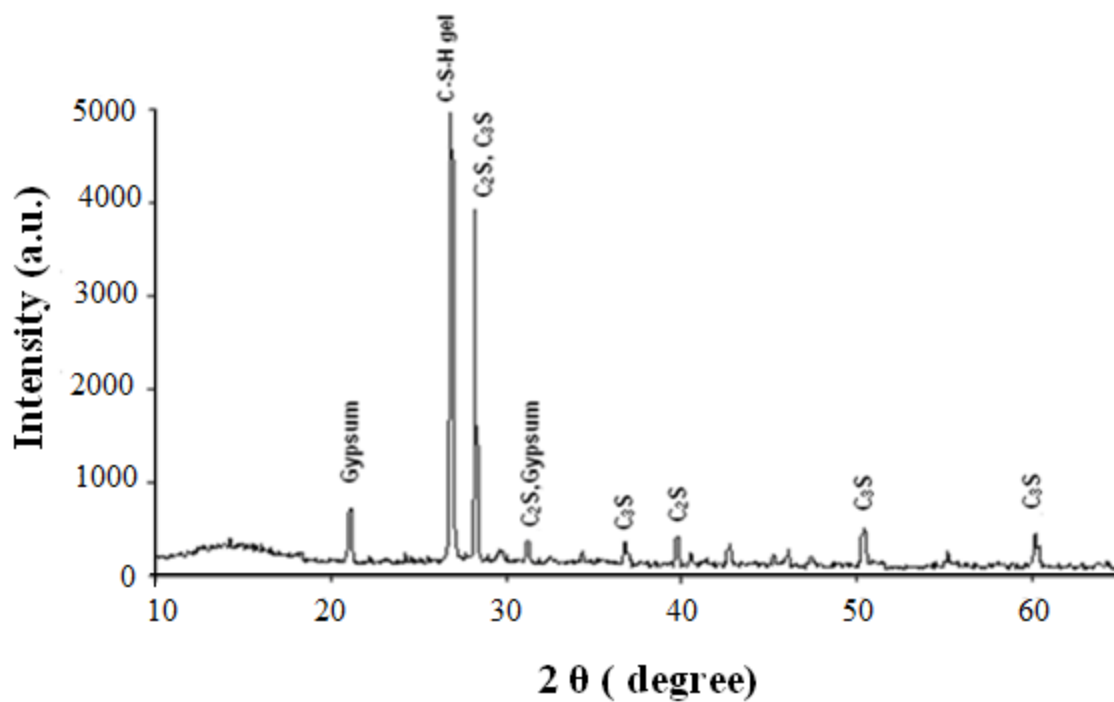


Figure 4.10: XRD spectrum of D tile sample

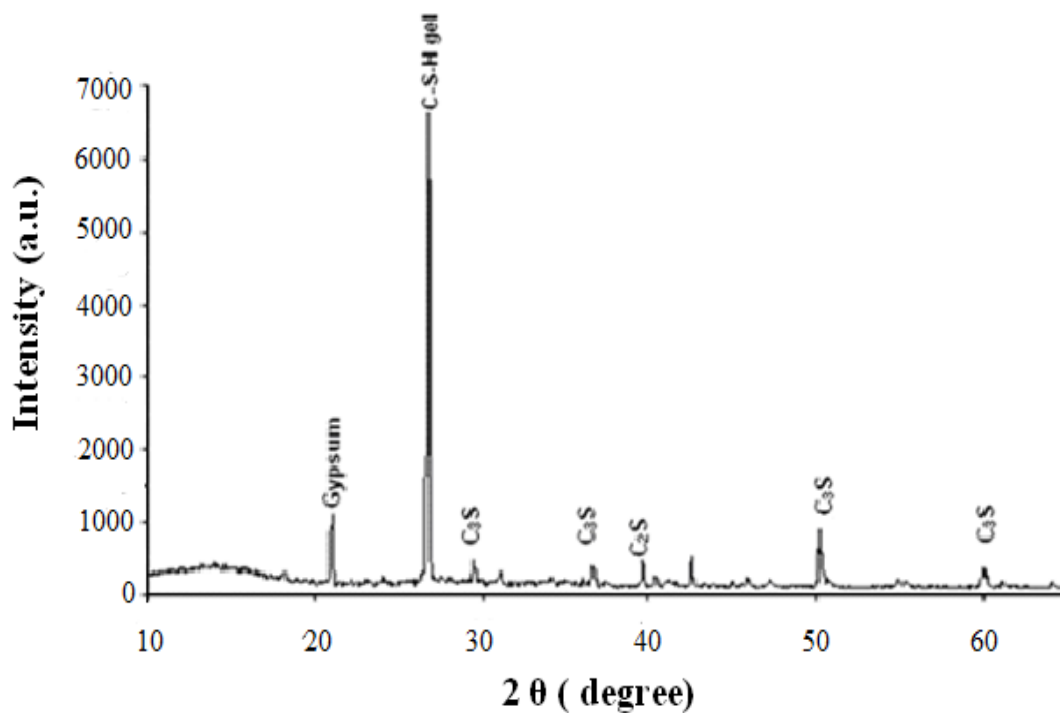


Figure 4.11: XRD spectrum of F tile sample

After 28 days, the compressive strength of tiles increases up to 50 MPa, which is required in case of heavy traffic area (e.g. bus terminals, industrial complexes, roads on expansive soils, factory floor, service stations, industrial pavements etc). A minimum 100 mm thickness is required on the tiles to achieve a compressive strength of 50 MPa according to IS 15658-2006. However, in this study, the requisite strength of tiles for heavy traffic area is achieved at 60 mm. As a result, the production cost of tiles can be reduced.

4.3.4 Cost analysis

In this study, transportation and labor charges are not accounted because it will be same in cement concrete mix and cement sludge concrete mix. Hence, only materials price has been used for the monetary value analysis study.

The cost analysis study is done in two ways:

Case 1: The cost of Blank tile (60 mm) is compared with sludge cement concrete mix tile (10% sludge).

Case 2: The cement concrete mix tile of 100 mm thickness is compared with sludge cement concrete mix tile (10% sludge) as both are having the same compressive strength (50 MPa).

Case 1:

Cost of cement = Rs 4.8/kg

Cost of sand = Rs 2/kg

Cost of stone grit = Rs 2/kg

Area of Dumbbell tile = 275 cm²

Volume of 60 mm tiles = 1650 cm³

Density of tile = 2.5 g/cm³

Therefore, Weight of tile = 4.12 kg

Weight of cement = 0.59 kg

Weight of sand = 1.18 kg

Weight of stone grit = 2.36

Cost of per tile for 60 mm thickness = Rs 9.90

Cost of per tile by using 10% sludge = Rs. 9.62

Therefore, Rs. 282 can be saved in per 1000 tiles by using 10% sludge in concrete mix of pavement tiles.

Case 2:

Area of Dumbbell tile = 275 cm^2

Volume of 100 mm tiles = 2750 cm^3

Density of tile = 2.5 g/cm^3

Therefore, Weight of tile = 6.87 kg

Weight of cement = 0.98 kg

Weight of sand = 1.96 kg

Weight of stone grit = 3.92

Cost of per tile by using 10% sludge = Rs. 9.62

Cost of per tile for 100 mm thickness = Rs 16.5

Therefore, Rs. 688 can be saved in per 100 tiles by using 10% sludge in the concrete mixture of pavement tiles in a heavy traffic area.

4.3.5 Discussions

The analysis of pickling sludge (Table 4.11) and cement (Table 4.13) are homogenous in term of chemical composition as both materials contain CaO, Fe₂O₃, MgO, SiO₂, and Al₂O₃ as their main components. Therefore, we have tried to replace cement with pickling sludge in the concrete mix. The result of sieve analysis of fine aggregate confirms that the sand fit in the grading zone 3. A special type of coarse aggregate is used for the production of concrete for pavement tiles. The commercial name of the gravel is zero size. It is observed from the physical test of tiles that the pickling sludge can be used in as partial replacement of cement without affecting the quality of pavement tiles. The compressive strength of the cement–sludge pavement tiles have been found to increase with the addition of sludge (29 to 50 MPa) as the replacement of cement up to 10% due to CSH formation. The negligible concentration of Fe was present in leachate as per US EPA TCLP test of cement–sludge pavement tiles. Hence, these tiles can be safely used on the footpath. This will not only solve the disposal problem but also decrease the manufacturing cost Rs. 688 per 100 tiles by using 10% sludge in a concrete mix of pavement tiles in a heavy traffic area.

Reference

- Bhattacharyya JK, Shekdar AV, Gaikwad SA (2004). Recyclability of some major industrial solid wastes. *Journal of Indian Association for Environmental Mangement*, 3: 71–75.
- Bolan N, Kunhikrishnan A, Thangarajan R, Kumpiene J, Park J, Makino T, Kirkham MB, Scheckel K (2014). Remediation of heavy metalloids contaminated soils--to mobilize or to immobilize? *J Hazard Mater*, 266: 141-66
- Brown S. L., Henry C. L., Chaney R., Compton H., DeVolder P. S. (2003). Using municipal biosolids in combination with other residuals to restore metal-contaminated mining areas. *Plant Soil*, 249: 203–215.
- Brunori C., Cremisini C., Massanisso P., Pinto V., Torricelli L (2005). Reuse of treated red mud bauxite waste: Studies on environmental compatibility. *J. Hazard. Mater.*, 1: 55–63.
- Cholpecka A., Adriano D. C. (1996). Influence of zeolite, apatite, and Fe-oxide on Cd and Pb uptake by crops. *Sci. Total Environ.*, 207: 195–206.
- Cocker KM, Evans DE, and Hodson MJ (1998). The amelioration of aluminum toxicity by silicon in higher plants: solution chemistry or an in planta mechanism? *Physiol. Plant*, 104: 608-614.
- Edwards R., Rebedea I., Lepp N. W., Lovell A. J.(1999). An investigation into the mechanism by which synthetic zeolites reduce labile metal concentrations in soils. *Environ. Geochem.*, 21: 157–173.
- Francisco Antonio Monteiro, Roberta Corrêa Nogueirol, Leônidas Carrijo Azevedo Melo , Adriana Guirado Artur & Fabiana da Rocha (2011). Effect of Barium on Growth and Macronutrient Nutrition in Tanzania Guineagrass Grown in Nutrient Solution, *Communications in Soil Science and Plant Analysis*, 42(13): 1510-1521.
- Friessl W., Lombi E., Horak O., Wenzel W. W (2003). Immobilisation of heavy metals in soils using inorganic amendments in a greenhouse study. *J. Plant Nutr. Soil Sci.*, 166: 191–196.

Galvez J.L., Javier D., Carlos N., Federico C.M. (2008). Hydrolysis of Iron and Chromium Fluorides: Mechanism and Kinetics, *Journal of Hazardous Materials*, 154: 135-145.

Gazey C. and Davies S. (2009), *Soil acidity: A guide for WA farmers and consultants*, The Department of Agriculture and Food, Western Australia, Bulletin 4784. ISSN 1833-7246.

Grag Neera and Singhal Priyanka (2011). Arsenic toxicity in crop plants: physioheightical effects and tolerance mechanisms. *Environmental Chemistry Letters*, 9(3): 303-321.

Gworek B (1992). Inactivation of cadmium in contaminated soils using synthetic zeolites. *Environ Pollut.*, 75: 269–271.

Haidouti C (1997). Inactivation of mercury in contaminated soils using natural zeolites. *Sci. Total Environ.*, 208: 105–109.

Hartley W., Edwards R., Lepp N. W. (2004). Arsenic and heavy metal mobility in iron oxide amended contaminated soils as evaluated by short and long term leaching tests. *Environ. Pollut.*, 131: 495–504.

Hsing HJ, Wang FK, Chiang PC, Yang WF (2004). Hazardous wastes transboundary movement management: a case study in Taiwan. *Resources, Conservation and Recycling*, 40: 329–341.

http://www.eisbc.org/Definition_of_Indian_SMEs.aspx :- Dated 23April 2014

<http://www.ncagr.gov/cyber/kidswrld/plant/nutrient.htm>: Dated: - 12th Nov 2013

Jian Feng Ma (2004). Role of Silicon in Enhancing the Resistance of Plants to Biotic and Abiotic Stresses. *Soil Sci. Plant Nutr.*, 50 (1): 11 - 18.

Jones Benton J., Jr., *Plant Nutrition Manual*, CRC Press - (1997) ISBN 188401531X, 9781884015311: 33-74.

Lin C. F., Lo S., Lin H., Lee Y (1998). Stabilization of cadmium contaminated soils using synthetic zeolites. *J. Hazard. Mater.*, 60: 217–226.

Lum KH, Stevens GW, Kentish SE (2012) The modeling of water and hydrochloric acid extraction by tri-n-butyl phosphate. *Chemical Engineering Science*, 84: 21–30.

Ma JF and Takahashi (2002). *Soil, Fertilizer, and Plant Silicon Research in Japan*. Elsevier Science, Amsterdam: ISBN: 978-0-444-51166-9.

Neumann D and zur Nieden U (2001) Silicon and heavy metal tolerance of higher plants. *Phytochemistry*, 56: 685-692.

Panneerselvam Selva Preetha, Palaniyandi Stalin (2014). Response of Maize to Soil Applied Zinc Fertilizer under Varying Available Zinc Status of Soil. *Indian Journal of Science and Technology*, 7(7): 939–944.

Raghu V (2001). Accumulation of elements in plants and soils in and around Mangampeta and Vemula barite mining areas, Cuddapah District, Andhra Pradesh India. *Environ Geol*, 40: 1265–1277.

Rakhshae R, Giahi M, Pourahmad A (2009). Studying effect of cell wall's carboxyl-carboxylate ratio change of *Lemna minor* to remove heavy metals from aqueous solution. *J Hazard Mater*, 163:165–173.

Ryuichi Suwa, Krish Jayachandran, Nguyen Tran Nguyen , Abdellah Boulenouar Kounosuke Fujita , Hirofumi Saneoka (2008). Barium Toxicity Effects in Soybean Plants. *Arch Environ Contam Toxicol*, 55: 397–403.

Sabir B.B, Wild S and Bai J. (2001). Metakaolin and calcined clays as pozzolans for concrete: A review. *Cement and concrete composites*, 23: 441-454.

Saxena, M., and Dhimole, L. K. (2016). Utilization and value addition of copper tailing as an extender for the development of paints. *Journal Hazard Material*, B129 (1-3): 50–57.

Singhal Anupam, Prakash Satya and Tewari V.K. (2007). Trials on sludge of lime treated spent liquor of pickling unit for use in the cement concrete and its leaching characteristics. *Building and Environment*, 42: 196–202.

Singhal Anupam, Prakash Satya and Tewari V.K. (2008). Characterization of stainless steel pickling bath sludge and its solidification/stabilization. *Building and Environment*, 43: 1010–1015.

Thomas R. (2015). *Practical guide to ICP-MS*. Marcel Dekker, Inc., 270 Madison Avenue, New York, NY 10016, U.S.A. ISBN: 0-8247-5319-4.

Thomas, B. S., Anoop, S, and Kumar, V. S. (2012). Utilization of solid waste particles as aggregates in concrete. *Procedia Engineering*, 38: 3789–3796.

Thomas, B. S., Damare, A., and Gupta, R. C. (2013). Strength and durability characteristics of copper tailing concrete. *Construction Building Material*, 48: 894–900

Williams DE and Vlamis J (1957). The effect of silicon on yield and manganese-54 uptake and distribution in the leaves of barley grown in culture solutions. *Plant Physiol*, 32: 404-409.

Zheng Miao Xie & Chang Yong Huang (1998). Control of arsenic toxicity in rice plants grown on an arsenic polluted paddy soil. *Communications in Soil Science and Plant Analysis*, 29: 2471-2477.

Conclusions and Future Scope

This chapter reports the chief findings of research and its future scopes.

5.1 Conclusions

Pickling sludge is hazardous in nature, so it cannot be disposed of directly at the landfill sites. Leachate of this sludge harms both aquatic life and soil. Neutralization is the conventional and economic treatment method for the small-scale industries. The method is simple, no complex installation is needed, but it consumes a lot of chemicals. The main drawback of neutralization process is the cost of storage of the sludge. Sludge transportation and construction of lined disposal sites pose a severe problem. By solidification and stabilization sludge can be safely discarded. However, this method is limited by the growing need for landfills to store hazardous waste. Evaporation/crystallization and spray roasting require high initial installation cost and energy and it is not amenable to small-scale plant. Solvent extraction method has certain advantages and disadvantages. The advantages are (a) it is very flexible and (b) it permits to process effluent over a wide concentration range of metal ion. The disadvantages are (a) emulsion formation, (b) low efficiency, (c) loss of compounds and (d) laborious. Other methods, membrane separation, and low-temperature crystallization are costly and highly energy intensive. Therefore, in the present thesis emphasis are given to minimize and treat pickling liquor in economic and environmentally friendly way (biosorption) and utilize the pickling sludge.

SPL was treated with a different neutralizing agent and their combination for reducing the sludge generation. Three different neutralizing agents viz. Potassium hydroxide, Sodium hydroxide and Calcium hydroxide and their combinations have been used for the study of the sludge generation quantity in waste pickling liquor treatment. Sludge characterization has been done by XRD and XRF. Following conclusions are being drawn from the neutralization treatment process results:

- a) 100% Potassium hydroxide generated the lowest sludge, but the cost of Potassium hydroxide pellets is much higher than the Sodium hydroxide (the cost of Potassium hydroxide pellets is approx. 3 times of Sodium hydroxide pellets).
- b) The economic solution is to use 20% calcium hydroxide and 80% Sodium hydroxide for SPL treatment without much affecting the quality of treatment.
- c) Lower sludge generation will result in lower cost of sludge handling, i.e. sludge collection, transportation, and disposal arrangement.

- d) Some amount of sludge can be used as fertilizer in the plantation where soil has high acidity.

An attempt has been made to treat SPL by an environmentally friendly method. Biosorption has many advantages over chemical methods. Biosorption is accomplished at a lower cost than conventional treatment methods. It has a higher efficiency. The amount of sludge produced is reduced in biosorption process. With this aim, Spent pickling was treated with different low-cost agriculture waste (Wheat and Rice husk, Sawdust and banana leave) and microalgae *Scenedesmus* Sp. Unfortunately, none of the agricultural waste able to treat the SPL may be due to high compaction. Hence, *Scenedesmus* sp. was selected for treatment process because research shows that it has the potential for treatment of domestic wastewater, Zinc and Cadmium loaded industrial wastewater. The optimum pH for removal of Fe (II) was 6.0, while the contact time was 60 min at room 25-28 °C temperature. The nature of biosorbent and metal ion interaction was evaluated by infrared (IR) technique. The experimental results lead to following conclusions:

- a) IR analysis of bacterial biomass revealed the presence of amino and hydroxyl groups, which are responsible for biosorption of Fe (II).
- b) The biosorption isotherms fitted well with Freundlich isotherm than Langmuir model with a correlation coefficient ($r^2 = 0.994$). The magnitude of biosorption capacity ($K = 1.43$) and biosorption intensity ($n = 1.179$) represents high uptake of Fe (II) ions from solution by microalgal biomass and multilayer deposition of iron ion species on the algal surface.
- c) The biosorption kinetic data were fitted well with the pseudo-second-order kinetic model and confirming the chemisorption reaction of iron on the algal surface.
- d) Continuous adsorption studies revealed that microalgae (*Scenedesmus* sp.) could be successfully used as biosorbent for treating spent pickling liquor in large scale industries as well.

Pickling sludge disposal is a huge problem, as we know that land disposal restrictions are becoming ever increasingly strict, driven by the technical, regulatory and political considerations. Hence, an attempt has been made to investigate the feasibility of utilizing the industrial waste as fertilizer for ornamental plant and partial substitute of cement in pavement

tiles. The possibility of reuse of copper tailings and pickling sludge as fertilizers was verified through the experiment. The experiment results have found following conclusions:

- a) These industrial wastes have the potential to be used as fertilizing agents in ornamental plants.
- b) The sample containing copper tailings and pickling waste had the most profound effect. Pickling sludge, when used alone, hindered the growth of the plants, but when used along with copper tailings produced positive results.
- c) Copper tailing along with pickling sludge could be used as the fertilizing agent.
- d) The heavy metal present in pickling sludge and copper tailing does not have any deprived effect on plant growth and its metal uptake.
- e) Moreover, pickling sludge and copper tailing reduce the uptake of barium contaminant due to presence of calcium (Ca) and magnesium (Mg)

The analysis of pickling sludge and cement are homogenous in term of chemical composition as both materials contain CaO, Fe₂O₃, MgO, SiO₂, and Al₂O₃ as their main components. Therefore, an effort has been made to partial replace cement with pickling sludge in the concrete mix. The experimental results reached to following conclusions:

- a) The compressive strength of the cement–sludge pavement tiles have been found to increase with the addition of sludge as the replacement of cement up to 10% due to C-S-H formation.
- b) Negligible Fe concentration was present in leachate as per US EPA TCLP test of cement–sludge pavement tiles. Hence, these tiles can be safely used on the footpath.
- c) This will not only solve the disposal problem but also decrease the manufacturing cost.

Limitation: The percentage of sludge can be increased more than 10% in tiles because the strength of the tiles is enhanced by increasing the percentage of sludge. However, due to complexity in procuring the pickling solution from the industries, we are not able to further carry out the experiments.

Although biosorption process is an economical and green method for treatment of spent pickling liquor, the metal-loaded exhaust microalgae require suitable disposal. Disposal will increase the burden on the environment. Therefore, we consider that an option much more suitable for the metal-loaded exhaust microalgae could be their use as fertilizer for plants. The microalgae consist of organic compounds and iron is one of the micronutrients for plants.

5.2 Further scope of the work

There is a possibility to undertake following as an extension of this study.

1. The percentage of sludge can be increased in the concrete-sludge mix above 10% until it retards the properties of tiles.
2. Application of exhaust biomass produced after the biosorption treatment of SPL.

Annexure A: Status of hazardous waste generation in India

State	Quantity of Hazardous waste generation (MTA)			
	Recyclable	Incinerable	Landfillable	Total
Andhra Pradesh	313217	31660	211442	556319
Assam	7480	8	3252	10732
Bihar	73	9	3357	3439
Chandigarh	723	NA	232	955
Chhattisgarh	283213	6897	5277	295387
Daman, Diu, Dadra & NH	56350	421	17219	73990
Delhi	203	1740	3338	59423
Goa	7614	8271	10763	26648
Gujarat	577037	108622	1107128	1792787
Haryana	4919	1429	30452	36800
Himachal Pradesh	4380	2248	35519	42147
Jammu and Kashmir	6867	141	9946	16954
Jharkhand	204236	9813	23135	237184
Karnataka	54490	3713	18366	76569
Kerala	23085	5069	690014	780015
Madhya Pradesh	127909	5036	34945	167890
Maharashtra	847442	152791	568135	1568368
Manipur	137	115	-	252

Meghalaya	6443	697	19	7159
Mizoram	12	Nil	90	102
Nagaland	11	Nil	61	72
Orissa	18427	4052	74351	96830
Pondicherry	36235	25	132	36392
Punjab	89481	14831	13601	117913
Rajasthan	84739	23025	165107	272871
Tamil Nadu	89593	4699	196002	401073
Tripura	237	30	0	267
Uttar Pradesh	117227	15697	36370	140146
Uttarakhand	11	580	17991	18582
West Bengal	126596	12583	120598	259777
Total	3088387	415794	2728326	6232507
	43.70%	6.67%	49.55%	100%

Annexure B: Specification of UV Spectrophotometer

Optical design	Double beam with and reference cuvette position; creny Turner Monochromator
Spectral Bandwidths (s)	1 nm
Light source	Xenon flash lamp
Detector	Dual silicon photodiodes
Scan ordinate modes	Absorbance, % transmittance, % reflectance, Kubelka Munk, height(1/R), height(Abs), Abs*Factor, Intensity
Wavelength	150-1100 nm

Annexure C: Acid Soil Region (ASR) in India

State	% of ASR
AP	20
Assam and N.E	80
HP	90
J&K	70
Karnataka	50
Kerala	90
Maharashtra	10
MP	20
Orissa	80
TN	20
UP	10
West Bengal	40

Source: Mahapatra Ishwar Chandra (1996). Publications and Information Division, Indian Council of Agricultural Research, New Delhi, India.

Annexure D: Specification of FTIR

Wavelength range	8300- 350 cm^{-1} optimized, proprietary KBr beamsplitter 7800-225 cm^{-1} with CsI beamsplitter option
Spectral resolution	0.4 cm^{-1} for 3028 cm^{-1} band in Methane
Wave number precision	0.008 cm^{-1} at 2000 cm^{-1}
Wave number accuracy	0.02 cm^{-1} at 2000 cm^{-1}
Optical system	Sealed and desiccated optical unit. Vibration isolated baseplate
Interferometer	Improved rotary Michelson interferometer for fast scanning, self-compensating for dynamic alignment changes due to a tilt and shear, incorporating high reflectivity, first surface aluminum coated optics
Detectors	DTGS (standard) Liquid nitrogen cooled mercury cadmium telluride (MCT) detector (option)

Annexure E: Specification of peristaltic pump

Model number	RH-P110S-50
RPM	0.5-49.5
Flowrate	6-3000 ml/hr
Tubing	3 cm dia (with 2 mm wall thickness)
Pressure	Upto 2 kg/sq.cm.
Power source	230 V, 50 Hz, AC
Motor	DC stepper motor
Temp range	0-50 °C
Dimentions	125x225x290 mm (HxWxD)
Weight	7 kg. (approx)
No of channels	1

Annexure F: Time optimization for Fe (II) reduction with five biosorbents

Sample code	Contact Time (min)	Adsorbent weight (g)	pH	Fe (II) in influent (mg/l)	Fe (II) in effluent (mg/l)	Reduction (%)
WH1	5	1	6	50	49.17	1.66
WH2	10	1	6	50	48.42	3.16
WH3	20	1	6	50	48.36	3.28
WH4	40	1	6	50	47.84	4.32
WH5	60	1	6	50	46.08	7.84
WH6	80	1	6	50	46.08	7.84
WH7	100	1	6	50	46.08	7.84
WH8	120	1	6	50	46.08	7.84
WH9	140	1	6	50	46.08	7.84
WH10	160	1	6	50	46.08	7.84
WH11	180	1	6	50	46.08	7.84
RH1	5	1	6	50	48.71	2.58
RH2	10	1	6	50	50.91	-1.82
RH3	20	1	6	50	51.39	-2.78
RH4	40	1	6	50	51.58	-3.16
RH5	60	1	6	50	51.61	-3.22
RH6	80	1	6	50	52.31	-4.62
RH7	100	1	6	50	52.82	-5.64
RH8	120	1	6	50	52.82	-5.64
RH9	140	1	6	50	52.82	-5.64
RH10	160	1	6	50	52.82	-5.64
RH11	180	1	6	50	52.82	-5.64
BH1	5	1	6	50	52.76	-5.52
BH2	10	1	6	50	52.67	-5.34
BH3	20	1	6	50	51.08	-2.16
BH4	40	1	6	50	51.39	-2.78
BH5	60	1	6	50	51.47	-2.94
BH6	80	1	6	50	51.32	-2.64
BH7	100	1	6	50	51.32	-2.64
BH8	120	1	6	50	51.32	-2.64
BH9	140	1	6	50	51.32	-2.64
BH10	160	1	6	50	51.32	-2.64
BH11	180	1	6	50	51.32	-2.64
SD1	5	1	6	50	48.23	3.54
SD2	10	1	6	50	48.57	2.86

SD3	20	1	6	50	48.89	2.22
SD4	40	1	6	50	48.45	3.1
SD5	60	1	6	50	48.12	3.76
SD6	80	1	6	50	48.12	3.76
SD7	100	1	6	50	48.12	3.76
SD8	120	1	6	50	48.12	3.76
SD9	140	1	6	50	48.12	3.76
SD10	160	1	6	50	48.12	3.76
SD11	180	1	6	50	48.12	3.76
SS1	5	1	6	50	45.32	9.36
SS2	10	1	6	50	42.12	15.76
SS3	20	1	6	50	36.14	27.72
SS4	40	1	6	50	35.1	29.8
SS5	60	1	6	50	32.18	35.64
SS6	80	1	6	50	34.32	31.36
SS7	100	1	6	50	34.32	31.36
SS8	120	1	6	50	34.32	31.36
SS9	140	1	6	50	34.32	31.36
SS10	160	1	6	50	34.32	31.36
SS11	180	1	6	50	34.32	31.36

WH- samples of Wheat Husk, RH- samples of Rice Husk, BH- samples of Banana peel Husk, SD- samples of Saw dust, SS- samples of *Scenedesmus* Sp.

Annexure G: Height of plant study on sludge as a fertilizer

September 2013



1

1A



2

2A

September 2013



3

3A



4

4A

Under Sunlight

- 1= Blank = Soil + fertilizer organic
- 2=Tailing=Copper sludge +soil
- 3=Sludge=Pickling sludge + soil
- 4=Mix=Tailing +Sludge

March 2014



1

1A



2

2A

March 2014



3

3A



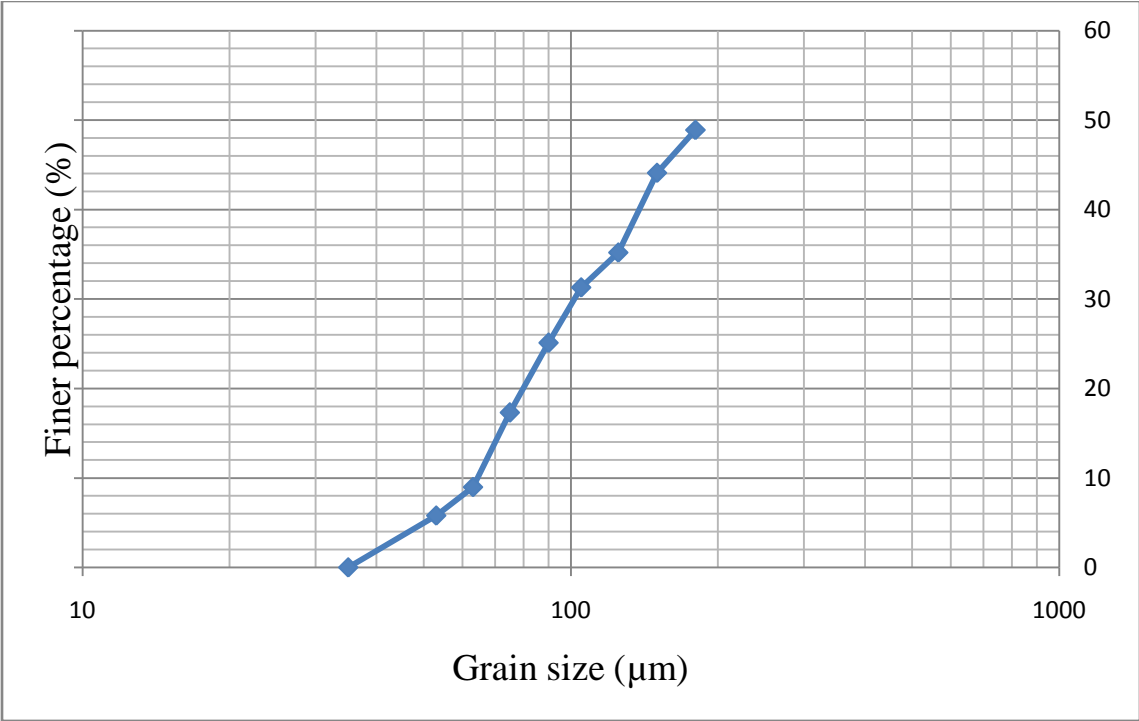
4

4A

Under Shadow

- 1A= Blank = soil + fertilizer organic
- 2A=Tailing=Copper sludge +soil
- 3A=Sludge=Pickling sludge + soil
- 4A=Mix=Tailing +Sludge

Annexure H: Particle size distribution graph of pickling sludge

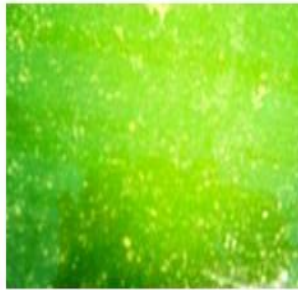


Annexure I: Batch and continuous study



Annexure J: Culture of *Scenedesmus* sp .algae

Culture of *Scenedesmus* sp .algae in Green House BITS Pilani, Pilani campus, Rajasthan



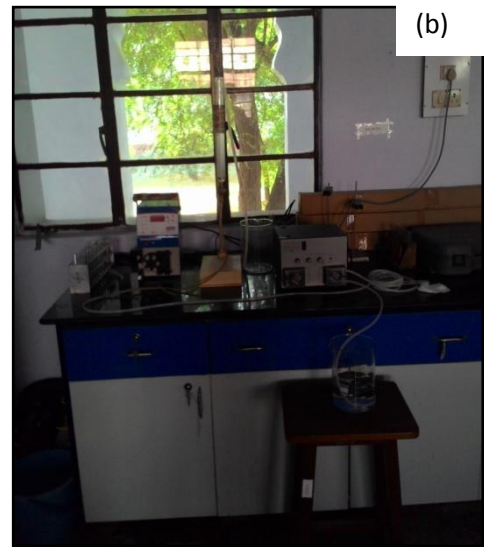
Packing of column for biosorption study



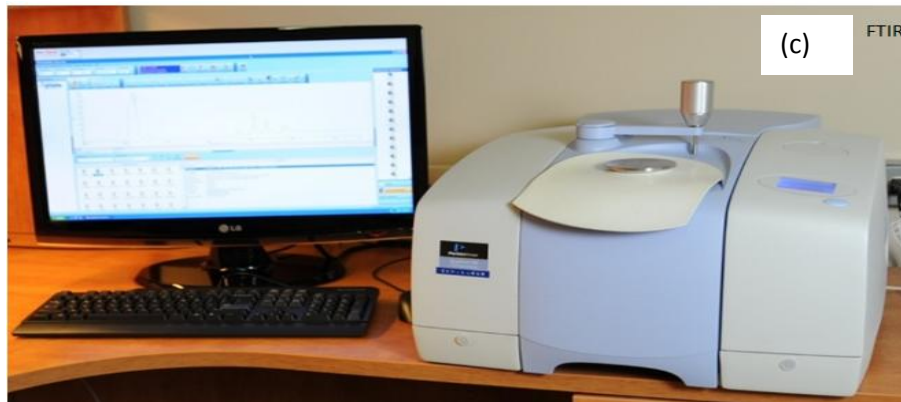
Annexure K: Picture of instruments used during thesis work



(a)



(b)



(c)

FTIR

(a) Bio-adsorption column study (b) Peristaltic pump (c) FTIR

Journals

- Anuradha Devi, Anupam Singhal, Rajiv Gupta, S.K. Verma, A N Singh "*Utilization of Industrial Waste as a Fertilizer in ornamental plants*" published online in Research Journal of Chemistry and Environment, Vol. 21 (4), 2017, pp 1-7.
 - (Impact factor : 0.636)
- Anuradha Devi, Anupam Singhal, Rajiv Gupta, Prasad Panzade "*A Study on treatment methods of spent pickling liquor generated by pickling process of mild steel*" published online in Clean Technologies and Environmental Policy , Vol 16(8) , 2014, pp 1515-1527.
 - (Impact factor : 3.33)
- Anuradha Devi, Anupam Singhal, Rajiv Gupta , S.K. Verma, Dr. Prasad Panzade, Martina Fernandes "*Economic Treatment Method of Waste Pickling Liquor for Micro, Small and Medium Scale Enterprises*" published in Journal of Water Pollution & Purification Research, Vol 1(1), 2014, pp 1-9. (eISSN: 2394-7306)
- Anuradha Devi, Anupam Singhal, Rajiv Gupta "*A Review on spent pickling liquor*" published in International Journal of Environmental Sciences, Vol 4(3), 2013, 284-295. (ISSN 0976 –4402)

Communicated

- Anuradha Devi, Anupam Singhal, Rajiv Gupta, S.K. Verma "*Biosorption of Fe(II) by Scenedesmus sp. in batch and Continuous systems*" Submitted in Indian Journal of Chemical Technology. Manuscript ID: IJCT-2529. (under review)
- Anuradha Devi, Rajiv Gupta, Anupam Singhal, S.K. Verma "*Application of pickling sludge in pavement tiles*" Submitted in Research Journal of Chemistry and Environment. Manuscript ID : RJCE- 2018-0044 (under review)

Conferences

- Anuradha Devi, Anupam Singhal, Rajiv Gupta, Arun Nihal Singh "***Hazardous Waste Management in Developing Countries***", International Conference on Integrated Solid Waste Management in Developing Countries, 11-12 April 2017, CSIR-NEERI Nagpur, India, pp-60.
- Anuradha Devi, Anupam Singhal, Rajiv Gupta, "***Treatment of Spent Pickling Liquor***", 4th International Conference on Recent Innovations in Science, Engineering and Management (ICRISEM-16) Venue: India International Centre, New Delhi, 20 March 2016. ISBN978-81-932074-6-8. pp 287-292.
- Anuradha Devi, Anupam Singhal, S.K Verma, Rajiv Gupta, A N Singh, 2015, "***A study on Industrial Waste as a Fertilizer***", 5th International Conference in Advances in Biotechnology, 10-11 March 2015 (Biotech 2015), IIT Kanpur, India. (ISSN: **2251-3159**)
- Anuradha Devi, Anupam Singhal, S.K Verma, Rajiv Gupta, A N Singh, Dr. Prasad Panzade, Martina Fernandes, 2014, "***Utilization of copper tailing and spent pickling liquor for improving the fertility of soil***", 4th International Conference in Advances in Biotechnology, 10-11 March 2014 (Biotech 2014), BITS Pilani Dubai campus , Dubai, pp 48-50. (ISSN: **2251-2489**)
- Bartik Pandal, Anupam Singhal and Anuradha Devi, 2013, "***An Overview of Utilization of Spent Pickling Sludge with Fly Ash in Cement Concrete Production***", The 5th Asia & Pacific Young Researchers & Graduates Symposium on Current Challenges in Structural Engineering, YRGS 2013, MNIT Jaipur, 15-16 Oct, pp 328-333

Brief biography of Candidate

Anuradha Devi completed her B.E. in Chemical Engineering from Jiwaji University, Gwalior, India in 2008. She has completed PG Diploma in Piping Engineering from IBPS Hyderabad in 2009. She has completed her M.Tech. in Environmental Process Design from Nirma University, Ahmedabad, India in 2011.



She has diverse exposure in Environmental Engineering. She worked in Petrochemical sector as a research trainee for one year. She also worked as a Designing engineer in SAI consulting engineers Pvt Ltd, at Ahmedabad for duration of one year. She was engaged in a Research project as a Project Fellow at Dept of Civil Engineering, BITS-Pilani, Pilani, India. Presently, she is pursuing her PhD at Dept of Civil Engineering, BITS-Pilani, Pilani, India.

Brief biography of Supervisor

Dr. Anupam Singhal had completed B.E. in Civil Engineering and M.E. in Environment Engineering from IIT Roorkee, India in 1992 & 1994 respectively. In year 2006, he was awarded with PhD from IIT Roorkee in Hazardous Waste Management.



He has diverse exposure in environmental engineering projects. He has worked as environmental engineer in industry & consultancy organization for eight years. He has designed many treatment plants for Water & Wastewater, Air pollution control systems and work as environmental consultant for many organizations. He has also carried out many EIA studies. Presently, he is working as Associate Professor in Dept. of Civil Engineering at BITS-Pilani. He is working on various projects funded by Govt. agencies. He has published many research papers in international/national journals/conferences of repute.

Brief biography of Co-Supervisor

Prof. Rajiv Gupta completed his B.E. and M.E. in Civil Engineering from BITS-Pilani India in 1983 and 1989 respectively. In 1995, he was awarded with PhD in Fluid Structure Interaction from BITS-Pilani, India.

Presently, he is working as a Senior Professor at Dept. of Civil Engineering at BITS-Pilani, India. In his last 3 decades of teaching and research, he has authored a number of books and course development material and published more than 150 research papers in India and abroad. His fields of interests are Energy- Water conservation, GIS and RS and Concrete Technology. He is executing various projects related to water domain of worth approx. 6 crores.



Brief biography of Co-Supervisor

Prof. Sanjay Kumar Verma obtained master's degree from Banaras Hindu University with specialization in cyanobacteria and applied phycology before completing PhD in the area of Environmental Biotechnology from the same university.



He worked as post-doctoral fellow at University of Hyderabad in the area of microbial and molecular genetics.

Currently he is working as professor in Department of Biological sciences and Dean of Academic Research Department at Birla Institute of Technology & Science, Pilani. Prof. Verma has handled several research projects related to bioremediation and biodegradation of toxic industrial waste, development of recombinant bacterial biosensor for environmental application, bioactive compounds from native cyanobacteria and higher plants from Shekhawati region & biodiesel production by microalgae, funded by DAE, CSIR, UGC, DST and WIPO. His major research interest lies in environmental biotechnology, microbial physiology & genetics. He has published many international and national research papers in reputed journals.