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Economical Treatment Method for Waste Pickling Liquor for Micro, Small and Medium Scale Enterprises

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Abstract

Waste pickling liquor is pertinent to hazardous waste. Various types of recovery and regeneration methods are used to recover and regenerate the acid and metals from waste pickling liquor. But these methods are sumptuous and not amenable for small scale industries. In a 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). This study has been undertaken to minimize the generation of the pickling sludge by different neutralizing agents and their combinations with economic valuation and also sludge characterization has been done. The results show that the treatment of pickling effluent with lime only is the economical solution but the quantity of sludge generation is on a higher side. However, the authors 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, i.e., sludge collection, transportation and disposal arrangement. The sludge characterization results show that the sludge generated by treatment of WPL requires further treatment before using it as a building material.

Keywords: *Pickling liquor, hazardous waste, sludge, precipitation, sludge characterization*

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INTRODUCTION

Rapid industrialization brings lot of pollution, whether it is air, land, water or noise. One of the major concerns in India is the increasing level of land pollution largely due to the uncontrolled disposal of industrial solids and hazardous waste. Hazardous waste can be defined as a waste if it exhibits any of the following: corrosivity, ignitability, reactivity or toxicity [1].

One of the major environmental problems for the steel industries comes from pickling plant waste. 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 into hot acidic solution either hydrochloric acid or sulfuric acid. Hydrochloric acid (HCl) is a preferred acid used in the pickling process because of the following advantages over sulfuric acid:

a) Faster cleaning rate at room temperature with lower dosages
b) Less chances of over pickling
c) Safer to handle

In an industrial pickling process, iron oxide dissolves in HCl acid; ferrous salt and water are formed according to the following reactions:

$$Fe_2O_3 + Fe + 6HCl \longrightarrow 3FeCl_2 + 3H_2O \quad (1)$$

$$Fe_3O_4 + Fe + 8HCl \longrightarrow 4FeCl_2 + 4H_2O \quad (2)$$

$$FeO + HCl \longrightarrow FeCl_2 + H_2O \quad (3)$$

HCl also reacts with the base steel by the following mechanism:

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2 \quad (4)$$

Spent baths must be disposed of because the efficiency of pickling decreases with increasing content of dissolved metal in the bath. Waste pickling liquor (WPL) is considered as hazardous waste and is specifically listed in Hazardous Waste (Management & Handling) Amendment Rules 2002 [2] due to its corrosive nature and presence of residual acid as well as high metal content.

In order to prevent the pollution of environment and to achieve the permissible effluent discharge limit, many techniques have been tried for WPL treatment The literature reported various processes for regeneration of acid and recovery of metals from waste pickling liquor. Metals (Fe, Cr and Ni) can be recovered from spent stainless steel pickling liquor by membrane electrolysis method. For higher nickel content recovery, iron has to be removed from the waste solution prior to electro deposition [3]. Pyrometallurgical process has been studied for total regeneration of both acid and metals in the form of oxide [4]. Inorganic acids regenerated by diffusion dialysis and effect of metals have been studied on their regeneration efficiency [5]. Fe is recovered from spent pickling by ultra-filtration [6] and solvent extraction method [7]. Iron and chromium are recovered in iron and chromium fluoride hydrate form, from mixed hydrofluoric and nitric acid solution by crystallization method [8]. Acid regeneration and metal recovery from various sources of pickling liquor by different methods have been discussed by [9, 10]. But these methods are sumptuous and not amenable to small scale industries. Sometimes the generated products such as iron salts and iron oxide offer little promise as a general solution to the problem because of a limited market of the compound [11].

The convenient and economical treatment method for waste pickling liquor in a developing country like India where approximately 30 million micro, small and medium enterprises (MSMEs) exist is precipitation/neutralization, under appropriate pH conditions [12, 13]. MSME sector of India is considered as the backbone of economy contributing 45% of the industrial output, 40% of India's exports and produce more than 8000 quality products for the Indian and international markets [14]. 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 increases the treatment cost. In the normal practice, sludge is disposed of at the sides of roads and railway track to fill low lying areas. This may cause serious health hazard. 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. Economic evaluation of the treatment process is carried out and also sludge characterization is done by X-ray diffraction (XRD) and X-Ray fluorescence (XRF) methods. A similar type of study was done by Singhal *et al.* in 2006, where calcium oxide and sodium hydroxide with their combination for the neutralization of pickling were studied [15].

MATERIALS AND METHODS

The pickling effluent samples were collected from steel industry where HCl is used for pickling of mild steel. Waste pickling acid (WPL) was taken for the study. Pickling effluent was characterized as per the standard methods [16] and the results obtained are given in Table 1. In normal practice, lime is used for treatment of WPL and it generates lots of sludge. Therefore, lime is used as base for comparing the generation of sludge and treatment cost.

Table 1: *Characterization of Pickling Effluent.*

Parameter	Value	Parameter	Value
pH	0.37	Chemical oxygen demand (COD) mg/L	5785
Electrical conductivity (EC) mS/cm	20	Iron g/L	82
Temperature, ºC	32	Chloride g/L	92
Total dissolved solids (TDS) g/L	13		

Chemicals Used

Pickling effluent was treated with various neutralizing agents, viz., lime (CaO), sodium hydroxide (NaOH), potassium hydroxide (KOH) and their various combinations. Lime purity = 80% as CaO, NaOH = 97%, KOH = 84% have been taken. In the treatment of pickling effluent, first of all pH was raised up to 12–14 by lime, NaOH, KOH or their combination. After that alum was used to decrease pH up to 7. Free settling was allowed. Procedure of the treatment process is depicted in Figure 1.

Various combinations used for optimization of treatment and their designations are given in Table 2.

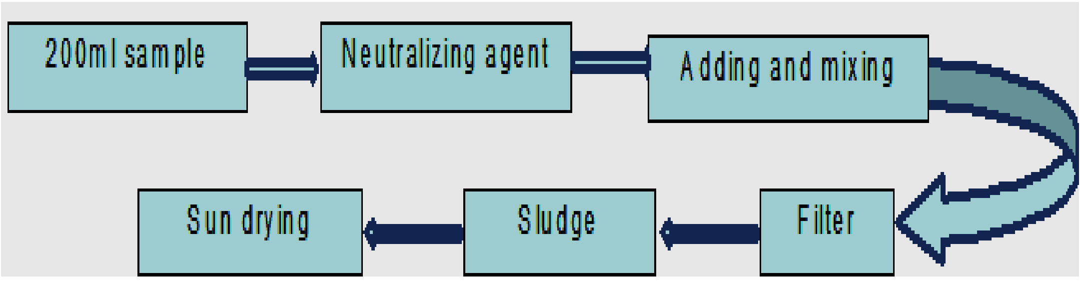

Fig. 1: *Sequence of Steps Involved in the Treatment Process.*

RESULTS AND DISCUSSION

Treated effluent was analyzed as per standard methods [16–19] and results are given in Table 3 and Figure 2. 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 WPL was treated with 100% lime only and brick-red color when WPL was treated with 100% NaOH and 100% KOH. The pH and dissolved oxygen (DO) value of treated WPL lie in the range of 6.5–7.8 and 2–4.3 mg/L respectively as given in Table 3. Graph of conductivity and total dissolved solids (TDS) is shown in Figure 2 and which confirms its linear relationship between them.

Treatment with neutralizing agents and their combination reduces TDS by 62–78%. Percentage reduction of TDS is given in Table 4. Highest reduction of TDS has been observed in treatment of lime only (78%) and lowest (62.31%) in KLH4 (80% KOH + 20% lime). 100% NaOH reduces TDS around 75% and 100% KOH reduces TDS approximately 68% in treated effluent.

Table 2: *Designation of Samples with Different Combinations for WPL Treatment.*

Sample code	Untreated pickling effluent volume (mL)	Calcium hydroxide (10% solution)	Sodium hydroxide (10% solution)	Potassium hydroxide (10% solution)
A	200	-	100%	-
B	200	-	-	100%
C	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%	-

Table 3: *Treated WPL Parameters.*

Sample code	pH	EC (mS/cm)	TDS (g/L)	DO (mg/L)
A	7.7	5.1	3.3	4.3
B	7.5	6.5	4.2	4.2
C	6.5	4.5	2.9	4
KLH1	7.12	6.00	3.9	2.5
KLH2	7.16	6.31	4.1	4.1
KLH3	7.18	6.46	4.2	2.2
KLH4	7.72	7.54	4.9	3
NLH1	6.67	4.92	3.2	2.4
NLH2	7.00	5.08	3.3	2.1
NLH3	7.12	6.00	3.9	2
NLH4	7.25	6.1	4.0	2.7

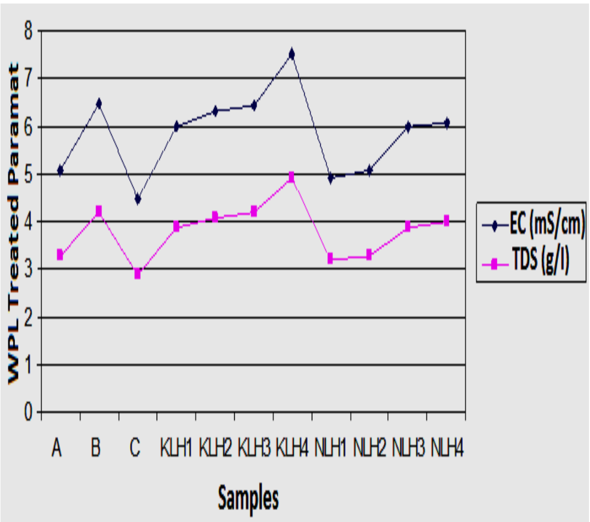

Fig. 2: *Graph Showing the EC & TDS Values vs Samples.*

Treatment with neutralizing agents and their combinations reduces TDS by 62–78%. Percentage reduction of TDS is given in Table 4. Highest reduction of TDS has been observed in treatment of lime only (78%) and lowest (62.31%) in KLH4 (80% KOH + 20% lime). 100% NaOH reduces TDS around 75% and 100% KOH reduces TDS approximately 68% in treated effluent.

Table 4: *Percentage of Total Dissolved Solids Removal.*

Sample code	TDS in WPL (g/L)	TDS in treated WPL (g/L)	% TDS removal
A	13	3.3	74.62
B	13	4.2	67.69
C	13	2.9	77.69
KLH1	13	3.9	70.00
KLH2	13	4.1	68.46
KLH3	13	4.2	67.69
KLH4	13	4.9	62.31
NLH1	13	3.2	75.38
NLH2	13	3.3	74.62
NLH3	13	3.9	70.00
NLH4	13	4	69.23

Sludge Generation

Sludge generation quantity during treatment of WPL by various neutralizing agents and their combination results is given in Table 5. Sample C which is 100% lime is taken as the base for comparison of sludge generation and treatment cost. It can be observed from Table 5 that the minimum sludge quantity is generated when WPL is treated with 100% KOH and maximum with 100% lime. A 30% reduction of sludge generation quantity has been observed in comparison to lime only when WPL is treated with NaOH only. 100% KOH reduces around 59.5% sludge generation quantity in comparison to 100% lime. Sludge reduction percentage increases from 11–56% in treatment of WPL, if the volume of KOH increases in combination of lime and KOH. In combination of lime and NaOH, sludge reduction increases from 25–33% by increasing the volume of NaOH.

Table 5: *Sludge Generated.*

Sample code	Sludge generation in treatment of pickling effluent (quantity 200 mL)		Percentage reduction in sludge generation
A	13	g	35.00
B	8.1	g	59.50
C	20	g	Base
KLH1	17.83	g	10.85
KLH2	13.68	g	31.60
KLH3	13.98	g	30.10
KLH4	8.85	g	55.75
NLH1	14.94	g	25.30
NLH2	14.35	g	28.25
NLH3	13.6	g	32.00
NLH4	13.44	g	32.80

Economic Analysis

In this section, cost of treatment of WPL with lime, NaOH, KOH and their combinations is discussed. The chemicals which were used for treatment of WPL and their price are given below:

Cost of KOH pellets = Rs.0.62/g
Cost of NaOH pellets = Rs.0.228/g
Cost of alum = Rs.0.022/g
Cost of lime = Rs.0.03/g

Table 6 shows the cost of treatment of WPL with lime, NaOH, KOH and their combinations. Although minimum sludge is produced by 100% KOH but its cost of treatment is almost 18 times more than that of lime and four times more than that of NaOH. It can be concluded from Figure 3 and Table 6 that NLH4 (20% lime and 80% NaOH) which reduces sludge generation quantity 33%, is a viable economical solution for treatment of WPL.

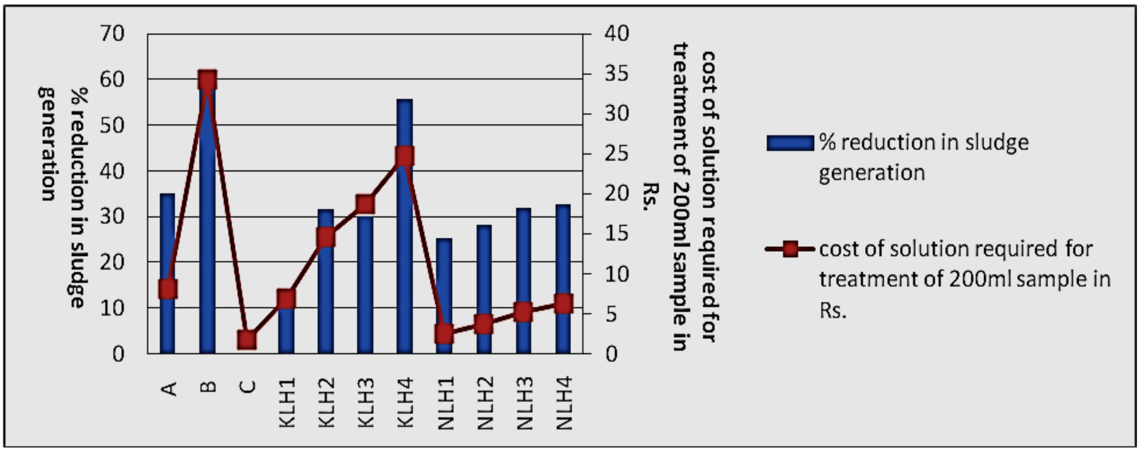

Fig. 3: *Graph between Percentage Reduction in Sludge Generation vs Cost of Solution Required for Treatment of 200 mL Sample.*

Table 6: *Cost of Treatment.*

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.
A	-	350	-	20	8.02
B	-	-	550	50	34.21
C	600	-	-	5	1.81
KLH1	400	-	90	30	6.85
KLH2	270	-	220	35	14.53
KLH3	225	-	290	40	18.74
KLH4	135	-	390	49	24.69
NLH1	320	65	-	20	2.49
NLH2	280	120	-	23	3.63
NLH3	210	200	-	25	5.25
NLH4	90	260	-	28	6.26

Treated Sludge Characterization

Three different types of neutralizing agents were used for treatment of WPL. The sludge generated in the treatment process has been characterized by XRD and XRF methods. Figure 4 shows the XRD pattern of sludge of sample A. Peaks of sample A sludge are found at 32°, 45.5°, 56.5° and 66°, which confirms that it is a sodium chloride (NaCl) compound.

From Figure 5, it can be observed that sample B sludge is potassium chloride as peaks are found at 28.5°, 40.6°, 50°, 59°, and 66° (JCPDS, 1972). Sample C sludge (calcium chloride) shows (Figure 6) the peaks at 23°, 29.6°, 31.2°, 47.7°, and 48.7° (JCPDS, 1972). XRD result details of samples A, B and C are given in Table 7.

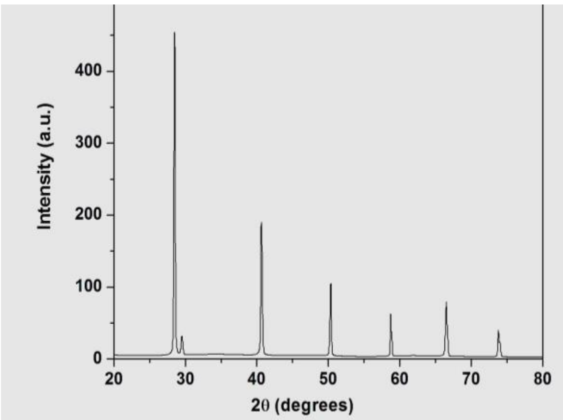

Fig. 4: *XRD Pattern of Sample.*

Sludge characterization of all samples of sludge has been done by using XRF method and results are incorporated in Table 8. WPL treatment generated sludge contains high percentage of chloride (as shown by XRF results). So, it cannot be directly used for building purpose because according to IS: 3025-1964 the permissible limit for chloride is maximum 2000 ppm for plain concrete work and 1000 ppm for reinforced concrete work (Indian Standard, 1979). Consumption of calcium hydroxide is higher than potassuim and sodium hydroxide as the percentage of calcuim 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 is due to presence of impurities in mild steel and neutrilizing agent. It can be observed from results that the sludge generated in 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). So, some amount of sludge can be used as a fertilizer for plantation where soil has high acidity [20].

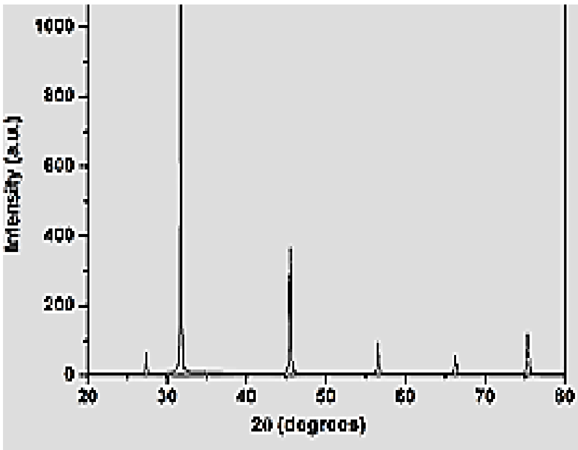

Fig. 5: *XRD Pattern of Sample B.*

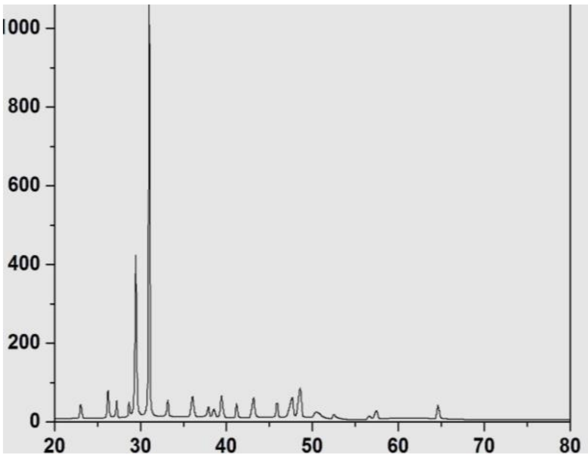

Fig. 6: *XRD Pattern of Sample C.*

Table 7: *Sludge Characterization by XRD.*

Sample	**2 Theta (2θ)**	**d(Å)**	**Compound identify**
Sample A	32°	2.8	NaCl
	45.5°	1.99	
	56.5°	1.63	
	66°	1.4	
Sample B	28.5	3.12	KCl
	40.6°	2.2	
	50°	1.81	
	59°	1.57	
	66°	1.4	
Sample C	23°	3.8	$CaCl_2$
	29.6°	3.01	
	31.2°	2.86	
	47.7°	1.90	
	48.7°	1.87	

Table 8: *Sludge Characterization by XRF.*

Sample	CaO%	O%	Cl%	MgO%	Fe_2O_3%	SiO_2%	Al_2O_3%	Na_2O%	K_2O%
Sample A	-	23.21	17.13	0.26	6.67	0.41	9.94	42.42	-
Sample B	-	26	13.31	0.13	6.34	0.11	8.85	-	55
Sample C	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	-

CONCLUSIONS

Three different neutralizing agents, viz., potassium hydroxide, sodium hydroxide and calcium hydroxide and their combinations have been used for study of the sludge generation quantity in waste pickling liquor treatment. Sludge characterization study has been done by XRD and XRF. The following conclusions can be drawn from the study:

a) 100% potassium hydroxide generated lowest sludge but the cost of potassium hydroxide pellets is much higher than sodium hydroxide (the cost of potassium hydroxide pellets is approximately three times of sodium hydroxide pellets).
b) The economical solution is to use 20% calcium hydroxide and 80% sodium hydroxide for WPL 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 plantations where soil has high acidity.
e) Sludge generated by treatment of WPL requires further treatment before using it as a building material.

REFERENCES

1. Wentz Charles A. *Hazardous Waste Management*, 2nd Edn. New Delhi: McGraw-Hill Inc; 1995.
2. *The Gazette of India*, Extraordinary, Part 11, Section 3, Sub section (ii), May 20, 2003. Published by Authority No. 471, MoEF, Notification, New Delhi.
3. Roemer Frank. *Metal Recovery from Spent Stainless Steel Pickling Solution Resources, Conservation & Recycling* 60. 2012. 72–7p.
4. Roemer F. Total regeneration of mixed pickling acid from stainless steel production-combination of nano-filtration and thermal processes. In: *Preprints of the International Conference and Exhibition for Filtration and Separation Technique*. 2009. 529–33p.
5. Oh SJ, Moon SH, Davis T. Effect of metal ion on diffusion dialysis of inorganic acids. *Journal Membrane Science*. 2000; 169(1): 95–105p.
6. Bern at Xavier. Recovery of iron (III) from aqueous stream by ultra filtration. *Desalination*. 2008; 221: 413–8p.
7. Agarwal A, Sahu KK, Kumar S. *Studies on solvent extraction of Fe (III) as a step conversion of a waste effluent to a value added product*. 2011; 92: 3105–11p.
8. Forsberg MK, Rasmuson CK. *Crystallization of metals fluoride hydrates from mixed hydrofluoric and nitric acid solution, Part 1, Fe (III) & Cr (III)*. 2010; 312(16-170): 2351–7p.
9. Agarwal A, Sahu KK. An overview of the recovery of acid from spent acidic solution from steel and electroplating industries. *J Hazard Mater*. 2009; 171(1-3): 61–75p.
10. Regal-Rostock M. A review on methods of regeneration of spent pickling solution from steel processing. *J Hazard Mater*. 2010; 177: 57–69p.
11. Tang B., Yuan L J, Shi TH, et al. Preparation of nano-sized magnetic particles from spent pickling liquors by

ultrasonic-assisted chemical co-precipitation. *J Hazard Mater*. 2009; 163: 1173–8p.
12. Mughal ST, Tahira S, Tayyaba A, et al. Treatment of Electroplating effluent. *J. Chem. Soc. Pak.* 2008; 30(1): 29–32p.
13. Galvez JL, Javier D, Carlos N, et al. Hydrolysis of iron and chromium fluorides: mechanism and kinetics. *J Hazard Mater*. 2008; 154: 135–45p.
14. http://www.eisbc.org/Definition_of_Indian_SMEs.aspx :- Dated 23April 2013.
15. Singhal A, Tewari VK, Prakash S. A Study on Sludge Minimization during the Treatment of Pickling Effluent. *Journal of Environment, Science and Engineering.* 2006; 48(2): 109–12p.
16. *Standard Methods for the Examination of Water and Wastewater*, 20th Edn. APHA, AWWA, WEF, Washington, DC; 1998.
17. *Powder diffraction file: Inorganic volume JCPDS.* International Centre for Diffraction Data. 1972.
18. *Indian Standard, Code of Practice for Plain and Reinforced Concrete.* Indian Standard Institution, New Delhi. 1979.
19. http://www.ncagr.gov/cyber/kidswrld/plant/nutrient.htm: Dated: - 12th Nov 2013.
20. Gazey C, Davies S. Soil acidity: A guide for WA farmers and consultants. *The Department of Agriculture and Food, Western Australia, Bulletin 4784*. 2009; ISSN 1833-7246.

