RECOVERY OF ACIDS FROM SPENT PICKLE LIQUOR OF A STEEL INDUSTRY BY ION-EXCHANGE ROUTE

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ABSTRACT

Spent pickle liquor (SPL) of steel industry is a major source of hazardous industrial wastes. Various methods have been investigated for the recovery of acid(s), Hydrochloric acid and Sulfuric acid from SPL. Each has got its own merits and demerits. Ion exchange method, a simple method has been used for the recovery of acid (s).In this study, the effect of ion exchange resin bed height (volume of resin) and contact time on the recovery of acid(s) was studied. It was found that the recovery of Sulfuric acid(s) was increased with increase in resin bed height and contact time. It was further found that after increasing the contact time from 5 to 10 minutes there was increase in acid recovery for Sulfuric acid. The resin LEWATIT-K 6362, an anionic resin has a good capacity of removal of iron from SPL of sulfuric and hydrochloric acids. Further it was observed that the resin volume required for the recovery of hydrochloric acid was less than that for sulfuric acid.

Key words: Ion exchange resin, Hydrochloric acid, Sulfuric acid, Spent pickle liquor

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INTRODUCTION

Spent Pickle liquor (SPL) of steel industry is a major source of hazardous industrial wastes. Pickling is removal of oxide layer formed on metal products by passing them through 15-20% HCl or H_2SO_4 at temperature up to 100^0C. SPL contains iron chloride / sulfates along with other metal ions such as zinc, chromium, nickel, iron(2-4). In actual practice SPL is neutralized with lime and generated sludge is land filled. But this causes land pollution [5-9,11,15,19]. Hence it has become necessary to develop alternative method for treating SPL.

The ion exchange resins have proven themselves in a wide variety of applications connected with the treatment and cleaning of waste water. Studies have been reported on use of ion-exchange resin for recovery of acid. M.J. Hatch and Dillon studied the acid retardation method for recovery of acid (s) fromSpent Pickle liquor (SPL) of steel industry [14]. M. Dejak and Kevin Munns studied the recovery of acid (s) by resin technology [22]. H. Tan reported acid-salt separation by selective adsorption with ion exchange resin [21]. Gülbas M.et. al. [23] also reported acid recovery by acid retardation. This research study deals with recovery of acid using LEWATIT-K 6362 ion exchange resin supplied by Lanxess India Ltd, Mumbai.

MATERIALS AND METHODS

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

Ion Exchange Resin (LEWATIT-K 6362) was procured from Lanxess India Ltd, Mumbai (India).It was yellow bead insoluble in cold water, with density1.08 g/cm^3 and pH<9 at concentration (w/w)10% (Figure 2.1).The resin is styrene-DVB based with functional group quaternary amine, cross linked polystyrene matrix strongly basic anionic type. It is strong oxidant. Total capacity 1.2 eq./l. The ionic form is Cl^-.

Fig. 2.1: Resin used for acid recovery

2.2 Experimental setup:

Figure 2.2: Experimental setup

It consists of chromatographic column, stand for fixing column and peristaltic pump for feeding the SPL and distilled water (Figure 2.2).

2.3 Methods:

2.3.1 Analysis of Spent Pickle liquor (SPL):

2.3.1.1 Determination of iron content and free acid in spent pickle liquor

The iron content and free acid in sulfuric acid spent pickle liquor was determined using the method given by Fred and Neil [3]. The method given by Fred and Neil [2] was used for iron content and free acid from hydrochloric acid spent pickle liquor.

2.3.1.2 Determination of heavy metals

The concentration of heavy metals like Fe, Zn, Pb, Cd, Ni and Cu present in spent pickle liquors were determined by the standard methods given in APHA (American Public Health Association) [1].

2.3.1.3 Determination of pH: pH of both spent pickle liquors were determined by usual standard methods.

2.3.2: Recovery of acid(s):

For recovery of the acid(s) the experimental set up as shown in figure 2.2 was used. First the column was packed with desired volume of resin (LEWATIT-K 6362). SPL was then pumped to column from the top and it was retained in the column for fixed time. Then the liquid which was collected from the bottom called as effluent sample was analyzed for free acid and iron. The resin was then backwashed by distilled water. This backwashed distilled water is eluted sample. The eluted sample was also analyzed for free acid and iron. The resin (LEWATIT-K 6362) has the property to absorb Sulfuric acid from Sulfuric acid containing SPL due to formation of bond between resin and Sulfuric acid while it has property to absorb Iron chloride due to formation of bond between resin and Iron chloride from Hydrochloric acid containing SPL.

3. RESULTS AND DISCUSSIONS

3.1 Analysis of Spent Pickle Liquor (SPL):

The analysis of SPL containing Hydrochloric acid and Sulfuric acid is reported in Table 3.1 and Table 3.2 respectively. It was found that the SPL contains Fe in large quantity followed by Zn and Cu. The other metals include Pb, Cd, and Ni in both SPL(s).The pH was found to be 0.72 and % free acid 9.2 for SPL containing Hydrochloric acid and pH was 1.21 and % free acid 49.1for SPL containing Sulfuric acid.

It was reported that the composition of SPL(s) from steel industry varies from process to process and depends on the process for which the acid(s) are used [13, 17].

Table 3.1 Analysis of SPL (Hydrochloric acid) from local steel industry

Component	Zn (mg/l)	Pb (mg/l)	Cd (mg/l)	Ni (mg/l)	pH	Fe (mg/l)	Cu (mg/l)	Free acid(%)
Concentration	157.589	13.565	0.82	6.498	0.72	443.673	46.259	9.2

Table 3.2 Analysis of SPL (Sulfuric acid) from local steel industry

Component	Zn (mg/l)	Pb (mg/l)	Cd (mg/l)	Ni (mg/l)	pH	Fe (mg/l)	Cu (mg/l)	Free acid(%)
Concentration	157.31	12.737	1.91	4.412	1.21	443.565	70.616	49.1

3.2 Recovery of acids:

3.2.1 Recovery of Sulfuric acid:

The effect of resin bed height and contact time for the recovery of Sulfuric Acid from SPL by ion exchange was investigated. The results of this are presented in Table 3.3 to 3.6.

Table 3.3: Sulfuric Acid recovery from SPL by ion exchange method
(Contact Time = 5 min., Volume of SPL= 10 ml)

Sr. No.	Resin Bed Height (cm)	% Free Sulfuric Acid in effluent sample(w/v)	% Free Sulfuric Acid in eluted sample(w/v)	% iron ineffluent sample (w/v)
1	4	19.8	25.5	0.040
2	5	16.4	30.7	0.040
3	6	12.1	34.2	0.041
4	7	10.0	35	0.043
5	8	9.4	35.6	0.044

Table 3.4: Sulfuric Acid recovery from SPL by ion exchange method
(Contact Time = 10 min. Volume of SPL= 10 ml)

Sr. No.	Resin Bed height (cm)	% Free Sulfuric Acid in effluent sample (w/v)	% Free Sulfuric Acid in eluted sample(w/v)	% iron in effluent sample (w/v)
1	4	18.5	28.8	0.041
2	5	16.8	31.5	0.041
3	6	15.6	33.0	0.041
4	7	14.9	34.0	0.042
5	8	9.8	39.2	0.043
6	12	8.3	40.1	0.044

Table 3.5 : Sulfuric Acid recovery from SPL by ion exchange method
(Contact Time = 5 min., Volume of SPL= 15 ml)

Sr. No.	Resin Bed height (cm)	% free Sulfuricacid in effluent sample(w/v)	% free Sulfuric acid in eluted sample(w/v)	% iron in effluent sample (w/v)
1	4	19.7	21.2	0.042
2	5	13.1	32.9	0.042
3	6	10.5	35.5	0.042
4	7	9.6	36.1	0.043
5	8	6.5	38.8	0.043

Table 3.6 : Sulfuric Acid recovery from SPL by ion exchange method
(Contact Time = 10 min., Volume of SPL= 15 ml)

Sr. No.	Resin Bed height (cm)	% free Sulfuricacid in effluent sample (w/v)	% free Sulfuric acid in eluted sample (w/v)	% iron ineffluent sample (w/v)
1	4	17.7	28.6	0.041
2	5	12.1	33.9	0.041
3	6	9.5	37.9	0.041
4	7	8.6	39.3	0.042
5	8	5.5	42.2	0.043

It was observed from Table 3.3 to 3.6 thatas resin bed height was increased %free acid in effluent sample decreased whereas % free acid in eluted sample was increased. Also as the contact time was increased from 5 to 10 minutes the % free acid in eluted sample was increased. Further it was observed that for increase in volume (15 ml)of the SPL, the contact time (5 to 10 minutes) was one of the factor for increase in recovery of the acid in the eluted sample compared to 10 ml of the SPL. This enhancement in the recovery of the acid in effluent might be attributed to the fact that sufficient time is needed for the absorption of the acid in the resin and the volume of the resin (bed height).

The % iron content in the effluent samples was found to vary from 0.040 to 0.044 (w/v) indicating that there was drastic decrease in the iron content and negligible amount of iron content was found in the eluted sample.

It has been reported by Dr. Stefan Neumann [24] that large quantities of sulfuric acid are used to anodize aluminium by the Eloxal process. Aluminium accumulates in the process bath, but can be tolerated up to a threshold concentration. Such kind of bath can be treated by acid retardation process in which a strongly basic ion exchange resin absorbs the acid while metal salts are allowed to pass through. This phenomenon is brought about through the effect of charge (Donnan Effect). The acid absorbed is then eluted which is free of metal salts. The same process was used in this study where iron salts are passed through the resin and sulfuric acid is absorbed in the resin and which was then eluted and found to be free of iron content, thus can be reused.

3.2.2 Recovery of Hydrochloric acid:

The effect of resin bed height and contact time of SPL for Hydrochloric acid recovery from SPL by ion exchange was investigated. The results of this are presented in Table 3.7 and Table 3.8

Table 3.7: Hydrochloric Acid recovery from SPL by ion exchange method
(Contact Time=5 min., Volume of SPL= 10 ml)

Sr. No.	Resin bed height (cm)	% free Hydrochloric acid in effluent sample (w/v)	% free Hydrochloric acid in eluted sample (w/v)	% iron in eluted sample (w/v)
1	3	8.1	0.8	0.040
2	4	8.1	0.8	0.040
3	8.5	8.2	0.9	0.041
4	8.8	8.2	0.9	0.041
5	9.2	8.2	0.9	0.042
6	12.8	8.2	0.9	0.043
7	15.4	8.2	0.9	0.044

Table 3.8: Hydrochloric Acid recovery from SPL by Ion Exchange method
(Contact Time=10 min., Volume of SPL= 10 ml)

Sr. No.	Resin Bed height (cm)	% free Hydrochloricacid in effluent sample(w/v)	% free Hydrochloric acid in eluted sample(w/v)	% iron in eluted sample (w/v)
1	3	8.0	0.8	0.040
2	4	8.1	0.9	0.040
3	8.5	8.2	0.9	0.041
4	8.8	8.2	0.9	0.041
5	9.2	8.2	0.9	0.042
6	12.8	8.2	0.9	0.043
7	15.4	8.2	0.9	0.044

From Table 3.7 and 3.8 it was observed that increase in bed height of resin up to 8.5 cm gave 8.2 % free hydrochloric acid in effluent sample and 0.9 % free hydrochloric acid in eluted sample. Further increase in bed height of the resin did not have any effect on % free hydrochloric acid in effluent as well as eluted sample. However, % iron in eluted sample varied from 0.040 to 0.044 (w/v). No iron content was found in effluent sample of hydrochloric acid indicating that the resin, LEWATIT-K 6362 has the capacity for the removal of iron. It has been reported by Maranon et.al. (25) that the anionic resins showed higher capacity for removing iron, especially Lewatit MP-500 and this capacity also increased with iron concentration.

4. CONCLUSION

It has been found that this resin, LEWATIT-K 6362 is suitable for the recovery of both sulfuric acid and hydrochloric acid from their respective SPL. Further it was found that the resin bed height (volume of resin) required for hydrochloric acid was less than that for sulfuric acid. Also it can be concluded that this resin has the good capacity for the removal of iron from the SPL and thus the acids can be reused in the process again.

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