Recovery of Sodium Sulphate from Process Waste of H-Acid Industry

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ABSTRACT

India is the second largest manufacturer of H-Acid in the world after China. H-acid is dye intermediate compound used in manufacturing of reactive dyes (To prepare dyeazo coupling in dye manufacturing). Due to its high pollution potential and high treatment cost, most of the countries not allowed H-Acid manufacturing in their countries. Due to usage of high strength acids and alkalies during manufacturing of H-acid, the combined wastewater stream is contaminated with high sulphate content. Sodium salts (Na_2SO_4) get accumulated in H-acid slurry. Decahydrate Sodium sulphate ($Na_2SO_4.10H_2O_4$) known as Glauber's salt and widely used in several industries like pharmaceutical, detergents, glass, paper etc. In H-Acid industry, Glauber's salt is contaminated with mother liquor of H-Acid and contains reddish tinge which hamper market value and industry has sent it to Hazardous Waste disposal site hence it is necessary to find-out economical and sustainable Sodium Sulphate recovery technique. We studied impact of Temperature, pH variation, use H_2O_2 oxidizing agent and coagulating agent to recover desired grade of sodium sulphate by removing unwanted impurities. It observed that, after double filtration of Glauber's salt slurry followed by oxidation and polyelectrolyte treatment then achieved 98% pure Sodium Sulphate crystals. This study is helpful to minimize waste, reduces treatment and disposal cost as well as reduce the production cost and product become economically viable to the industry.

Keyword: H-Acid, Sodium Sulfate,Glauber salt, Waste minimization, Recovery

I INTRODUCTION

Indian dyes and dye intermediates sector is vital sector and it accounts for more than half of the total export value of Indian chemical industry. As per working group report for 12th five year plan (2012-2017) submitted to Ex-planning Commission in November 2011, the dyes and dye intermediates sector has revealed a phenomenal growth in last 15 years and the exports increased from Rs. 100 Crores in 1986-87 to Rs. 7950 Crores in 2000-2001. Indian dyes and dye intermediates industry comprises of large scale manufacturers as well as medium or small scale manufacturers. In India, there are about 50 big manufacturers in organized sector and about 900 small units manufacturing dyes and dye intermediates chemicals. The total production of dyes in India is about 94,000 tons per year out of which 53,000 tons are exported. The total production of dye intermediates is about 250,000 tons out of which 120,000 tons are exported.

The steep rise in exports is due to increased exports to developed countries, which are finding it economical to import from third world countries as environmental regulations in developed countries have become more and more stringent. Indian dyes and dye intermediates industry has grabbed this opportunity without giving sufficient attention to our environment. A number of defaulting industries had closed by judiciary and regulating authorities because they were letting out hazardous wastes without proper treatment. The manufacturers have to compete with China who is flooding the world markets by dyes and dye intermediates at very low price.Most of the H-acid is exported, bringing in valuable foreign exchange to our country. Thus the challenge to Indian dyes and dye intermediates sector, it is necessary to find a balance between environment protection and economic development. To achieve this objective, it is essential to incorporate the principles of green chemistry and green engineering in this process.

Some of the large scale manufacturers are multinational companies and they have their own disposal facilities. Small scale manufacturers send their wastes to common disposal facilities. The process wastes from dyes and dye intermediates manufacture are iron sludge generated in iron-acid reduction, gypsum sludge and sodium sulphate/sulphite sludge. Many industries landfill these sludges without attempting to recover value added products from the same. Only few industries recover sodium sulphate/sulphite and aluminium hydroxide from their respective sludges. (Planning Commission report, 2011)

II H-ACID - DYE INTERMEDIATES

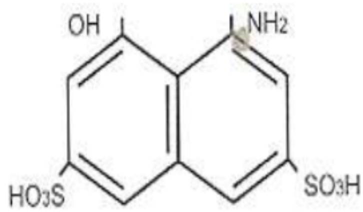
H-acid is one of the leading dye intermediates in the world, used in manufacture of black dyes. India is the second largest manufacturer of H-Acid in the world after China. H Acid is used in the manufacture of a large number of azo-dyes and pigments. Also it is widely used in detergents and in pharmaceutical preparations. H-acid is responsible for the most polluting industrial effluent in the dye and dye intermediate sector.

NAME OF PRODUCT
H-ACID

CHEMICAL NAME
1-Amino-8-Naphthalene-3, 6-Disulfonic.c Acid

SYNONYMS
1-Amino-8-Hydroxy Naphthalene3-6 Disulfonic Acid

FORMULA
$C_{10}H_9O_7NS_2$



Molecular Weight	319
Physical Appearance	Grayish Powder
Assay, by Nitrite Value	80% Minimum for Dry Powder 55% Minimum for Moist Cake
Insoluble (W/W)	0.5% Maximum
Iron Content (Acid Soluble)	500 PPM Maximum
Koach Acid	0.5% Maximum
Chromo Tropic	1.0% Maximum
Omega Acid	Traces
Solubility	Soluble in water and Dilute Alkaline Solution
Particle Size	100% (20 Mesh) 75% (60 Mesh)
USES	Intermediate for Dyestuffs

(Internet ref – Panoli Intermediates (India) Pvt. Limited)

III PROBLEMS OF H-ACID EFFLUENT

Manufacturing 1 kg of H-acid, results in the generation of 50 kg waste. In other words, it has an E-Factor of 50. The waste is of dark color, strong acidity and contains substituted derivatives of naphthalene compounds. These organic substances are toxic, non-biodegradable, difficult to decolorize and resistant to conventional treatment. It has a very high COD of 1,50,000.Having considered the ill effects of H-acid manufacturing process, currently most of the developed countries have banned it due to their stringent environmental norms. For this reason, the manufacturing was outsourced to countries like China and India where environmental norms are not as strict. (IGCW, 2014)

(a) Glauber's salt

Glauber's salt is common name for sodium sulfate decahydrate, $Na_2SO_4 \cdot 10H_2O$; it occurs as white or colorless monoclinic crystals. Upon exposure to fairly dry air it effloresces, forming powdery anhydrous sodium sulfate. Johann Glauber's salt is water soluble, has a salty, bitter taste, and is sometimes used in medicine as a mild laxative; it is also used in dyeing.

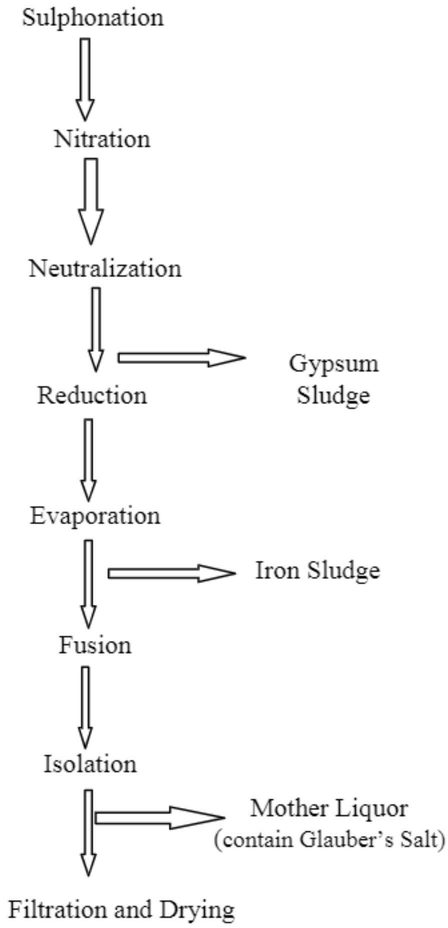


Fig. 1 – Manufacturing process of H-Acid

These are widely demanded in several industries like pharmaceutical, glass, paper and several other products manufacturing industries

(b) Study area

The study area selected for this project is M/s. Shree Hari Chemicals Export Ltd., Plot No. A-8, Mahad MIDC, Dist Raigad, Maharashtra (I).

(c) Need of the project

H-Acid is banned in most of the countries due to high pollution potential. The H-Acid is mostly manufactured in China and India. During Manufacturing of H-Acid, three type of waste mainly generated such as Gypsum sludge during neutralization, Iron sludge during evaporation and Mother Liquor during isolation process. Out of which gypsum and iron sludge has more economic value because gypsum is directly used as raw material in cement industry while Iron sludge is used in paint industry like manufacturing of red oxide. But mother liquor creates problem during treatment of mother liquor. In mother liquor having about 20 to 25% sodium sulphate salt is present in dissolved form. So it is necessary to recover sodium salt from mother liquor and convert it into commercial form to gain economical benefits. At present M/s. Shree Hari Chemicals Export Ltd. is sent this process waste i.e. Glauber's salt recovered from mother liquor at Common Hazardous Waste Treatment Storage and Disposal Facility (CHWTSDF) site and spends lots of money on disposal of this process waste. Hence it is necessary to find out economical and sustainable recovery technique of Sodium Sulfate to sale recovered sodium sulphate in market as valuable by-product or recycle in the process. This study is helpful to minimize waste, reduces disposal cost as well as earns economic benefit to the company.

Table 1
Characteristics of Mother Liquor

Sr. no.	Parameter	Value
1	pH	1.88
2	COD	86400 mg/l
3	TDS	242000 mg/l
4	Acidity	3%

Table 2
Physical Properties of Sodium Sulphate

Molecular formula	Na_2SO_4
Molecular weight	142.04gm/mole (anhydrous) 322.20gm /mole (decahydrate)
Appearance :	White crystalline solid
Odour	Odourless
Boiling point	1429°C(anhydrous)
Flashpoint	800°C
Melting point	884°C (anhydrous) 32.4°C (decahydrate)
Density	2.664gm/ml (anhydrous) 1.464gm/ml (decahydrate)
Refractive index	1.468 (anhydrous) 1.394 (decahydrate)
Solubility	Soluble in water, glycerol and hydrogen iodide and insoluble in ethanol
Use of Sodium Sulphate	• Sodium sulphate is used to dry an organic liquid • As filler in powdered home laundry detergents • As a fining agent which removes small air bubbles from molten glass • Glauber's salt, the decahydrate was used as a laxative which removes the certain drugs such as acetaminophen from the body • For de-frosting windows, in carpet fresheners, starch manufacture • As additive to cattle feed • In the manufacture of detergents and in the Kraft process of paper pulping • Used in tannery

(a) Recovery of Glauber's salt from Mother liquor of H-Acid

During manufacturing of 1 MT H-Acid 1.6 MT Mother liquor generated and in Mother liquor 20 to 24 % Glauber's Salt is present. The mother liquor having following characteristics,

It is known that Glauber's salt can be converted into anhydrous sodium sulphate, (Crystal White) which has a higher commercial value than Glauber's salt, effect the conversion of a relatively small proportion of the total sodium sulphate in the Glauber's salt to the anhydrous salt since only about 16 parts of the 4.4 parts of Na_2SO_4 contained in 100 parts of Glauber's salt (parts being by weight) are converted to anhydrous sodium sulphate on heating Glauber's salt to its transition point. (Kharat and et al, 2009)

To recover the Glauber salt from mother liquor, temperature of mother liquor reduces bellow 10°C then sodium salt starts crystallizing, the maximum salt present in Glauber salt is crystallized at 4°C. Excess liquid is removed by filtration with simple filter paper and crystallized salt collected and dried. This Glauber salt contains many impurities hence it has brownish colour tinge.

Fig. 2 - Recovery of Glaubers Salt from Mother liquor after temperature reduction

Fig. 1 - Recovered Glaubers Salt from mother liquor after filtration followed by air dyed/dried

Fig. 4 - Recovered Glaubers Salt crystals from mother liquor

Fig. 3 - Glaubers Salt after 1st filtration

(a) **Selection of simple technique for the removal of impurities** – For removal of brown colour tinge (impurities), we selected simple adsorption technique by filtering the salt solution through activated charcoal filter. For this process we selected charcoal based on sizes and iodine value of the charcoal. The characteristics of selected charcoal is as given below,

Characteristics	Charcoal type		
	Sample 1	Sample 2	Sample 3
Size	5-5.5 mm	1-1.5mm	2-2.5mm
Iodine value	800 mg/gm	1100 mg/gm	600 mg/gm

As iodine value of 2nd sample of activated charcoal was higher than other two charcoal samples, and size is also small, having higher surface area for adsoption, it was selected for the filtration process and it filled in specially designed glass column having 2 feet height and 3 inch diameter.

There are six different permeation and combination techniques selected for experiments. The procedure and results of experiments are described given below -

Experiment 1 - The 10gm of glaubers salt taken and dissolved in water and filtered through charcoal filter. The filtrate was evaporated and sodium sulphate crystals recovered but this crystals still having light brownish colour tinge. Hence again this crystal was dissolved in water and again filtered through charcoal filter and evaporated the solution at 100°C to 110°CtorecoverSodium Sulphate crystals.

Experiment 2- The 10gm of glaubers salt taken and dissolved in water and filtered through charcoal filter. The filtrate was evaporated and recovered sodium sulphate crystals but this crystals having slight colour tinge hence this crystal was again dissolved in water followed by H_2O_2 oxidizing treatment then filtered this solution through charcoal filter and evaporated it at 100°C to 110°C to recover Sodium Sulphate crystals.

Experiment 3:**-** The 10gm of glaubers salt taken and dissolved in water then oxidize the salt solution using H_2O_2as oxidizing agent followed by increases pH of solution up to 10 using NaOH (1N). Then pH of salt solution is neutralized by using diluted H_2SO_4 (1N) then it filtered through charcoal filter and evaporate this solution at 100°C to 110°C to recover Sodium Sulphate crystals.

Fig. 5 – Recovered Sodium Salphate after Experiment 6

Experiment 4:**-** The 10gm of glaubers salt taken and dissolved in water then oxidize the salt solution using H_2O_2followedby increases pH up to 10 using NaOH (1N) solution then use alum as coagulant agent to precipitate all impurities present in the salt solution. Then pH of salt solution is neutralized by using diluted H_2SO_4 (1N) then filtered this solution through charcoal filter and evaporate it at 100°C to 110°Cto recover Sodium Sulphate crystals.

Experiment 5:**-** The 10gm of glaubers salt taken and dissolved in water then oxidize the salt solution using H_2O_2followedby increases pH up to 10 using NaOH (1N) solution then use polyelectrolyte as coagulant agent to precipitate all impurities present in the salt solution. Then pH of salt solution is neutralized by using diluted H_2SO_4 (1 N) then filtered this solution through charcoal filter and evaporate this solution at 100°C to 110°C to recover Sodium Sulphate crystals.

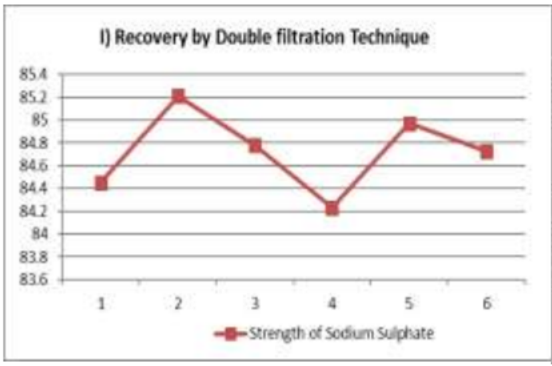
Experiment 6:**-** The 10gm of glaubers salt taken and dissolved in water then oxidize the salt solution using H_2O_2andfiltered through charcoal filter.The filtrate was evaporated at 100°C to 110°C and sodium sulphate crystals recovered. Again these recovered salts dissolved in water and adjust pH up to 10 using NaOH (1N) solution then use polyelectrolyte as coagulant agent to precipitate all impurities present in the salt solution. Then pH of salt solution is neutralized by using diluted H_2SO_4 (1N)then filtered this solution through charcoal filter and evaporate this solutionat 100°C to 110°Cto recover Sodium Sulphate crystals

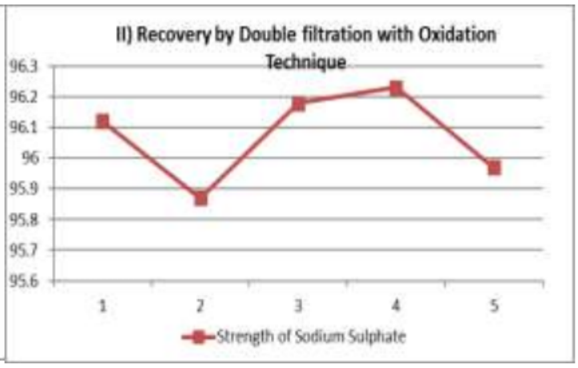
Then strength of all recovered sodium sulphate samples was checked by using titrimetric analysis with $BaCl_2$ and use Sodium Rhodizonateas an indicator. End point ?? The calculated strengths of sodium sulphate is as given below –

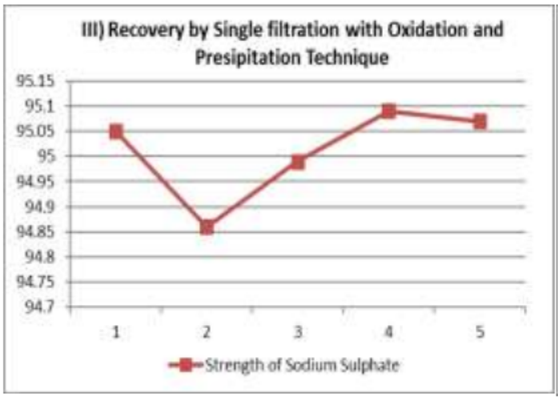
Table 1
Strength of recovered samples of Sodium Sulphate in %

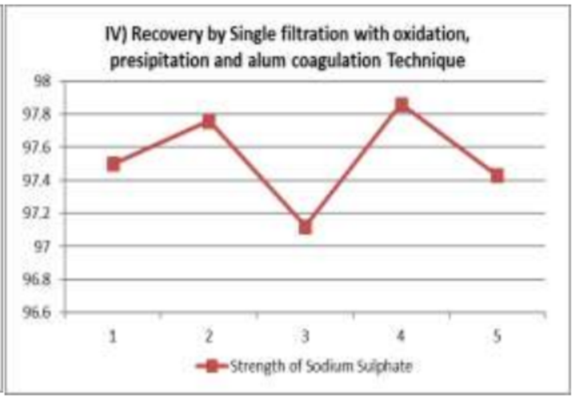
Sample Runs	Strength of Sodium sulphate in %					
	Experiment I	Experiment II	Experiment III	Experiment IV	Experiment V	Experiment VI
1	84.45	96.12	95.05	97.5	98.07	98.78
2	85.21	95.87	94.86	97.76	98.2	98.25
3	84.78	96.18	94.99	97.12	97.77	97.96
4	84.23	96.23	95.09	97.86	97.73	98.66
5	84.97	95.97	95.07	97.43	98.03	98.43
Average %	84.728	96.074	95.012	97.534	97.96	98.416

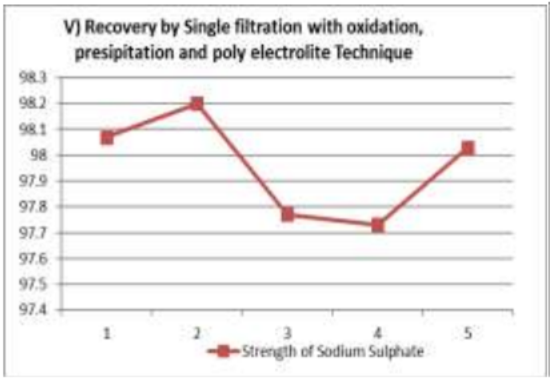
Graphical Representation as given below

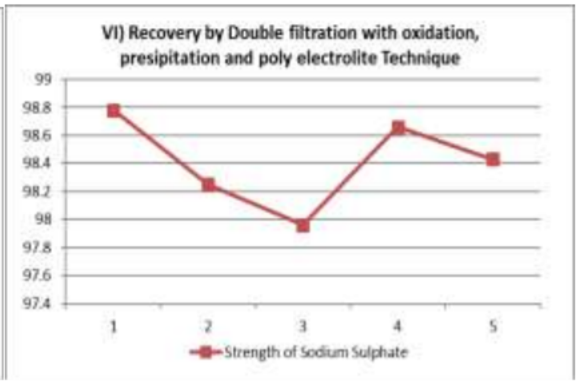


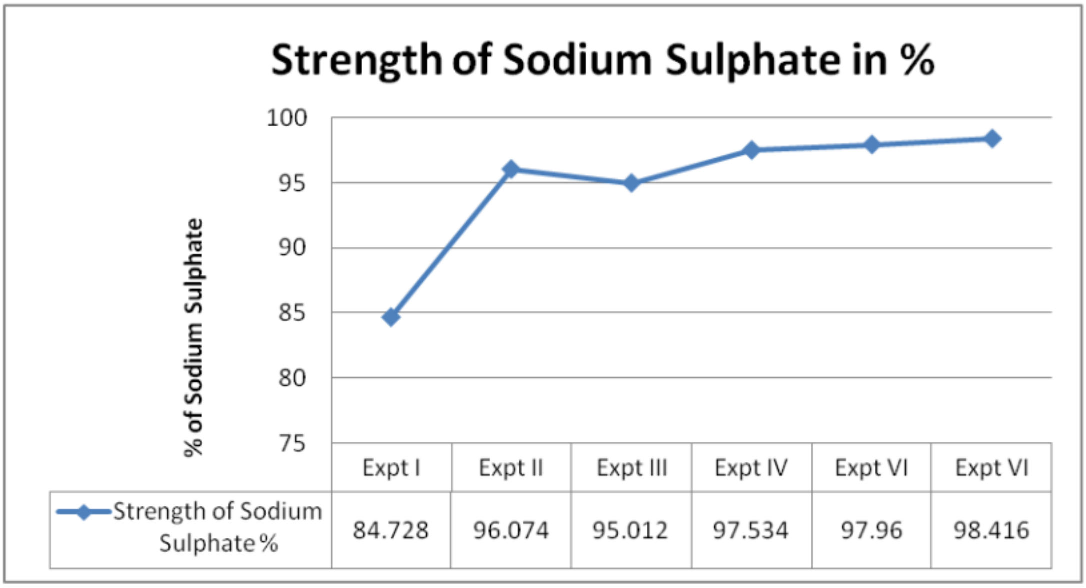












	Expt I	Expt II	Expt III	Expt IV	Expt VI	Expt VI
Strength of Sodium Sulphate %	84.728	96.074	95.012	97.534	97.96	98.416

IV CONCLUSION

As per analysis carried out, strength of Sodium Sulphate is achieved 84.72% in double filtration technique, 96.07% in double filtration followed by oxidation process, 95.01% in single filtration followed by oxidation then increase alkalinity followed by neutralization process, 97.53% in single filtration followed by oxidation and use Alum as coagulating agent, 97.96% in single filtration followed by oxidation and use Polyelectrolyte as coagulating agent while **98.41%** in double filtration followed by oxidation and use polyelectrolyte as coagulating agent.

Means double filtration followed by oxidation and polyelectrolyte treatment is showing higher strength recovery of Sodium sulphate i.e. 98% than other methods.

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