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The Efficient Process for Spent-caustic Wastewater Treatment

SeyedHadi Seyedin, Majid Hassanzadeganroudsari*

Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran.
Collage of Health and Biomedicine, Victoria University, Melbourne, VIC and Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran.

ABSTRACT: In this paper has been presented a new treatment method for spent caustic wastewater. Spent caustic is a waste industrial caustic solution that has become exhausted and is no longer useful. Spent caustics are made of sodium hydroxide or potassium hydroxide, water, and contaminants. The contaminants have consumed the majority of the sodiumor potassium hydroxide and thus the caustic liquor is spent, for example, in one common application H_2S gas is scrubbed by the liquid NaOH to form NaHS (aq) and H_2O (l), thus consuming the caustic. Spent caustics are malodorous wastewaters that are difficult to treat in conventional wastewater processes. Some kind of treatment technologies are disposed of by high dilution with biotreatment, deep well injection, incineration, wet air oxidation, Humid Peroxide Oxidation or other speciality processes. Most ethylene spent caustics are disposed of through wet air oxidation.

KEYWORDS: New Treatment Process, Wastewater, Spent Caustic, Sodium Hydroxide, Recovery.

I. INTRODUCTION

Sodium hydroxide (caustic) scrubbing solutions are commonly used in petrochemical and gas/petroleum refineries for the removal of acid components such as hydrogen sulfide, cresylic acids, mercaptan and naphthenic acids from the refined product streams [1]. Due to being hazardous, odorous, and/or corrosive components of spent caustic, handle and dispose of them, can be a challenge. Spent caustic streams may also have other characteristics that can create issues with conventional biological processes such as noxious odors, pH swings, foaming, or poor settling of biological solids [1]. Effluent requirements may be difficult to achieve because some spent caustic contaminants are not readily biodegradable. One of the key contributors to relatively high chemical oxygen demand (COD) and biological oxygen demand (BOD) is from the acid gas (both CO2 and H2S) and mercaptan removal system(s) typically using dilute caustic soda (NaOH) as the active reagent. The resultant waste stream is otherwise known as spent caustic. It's difficult to clean up and dispose of due to its toxic properties. Typically, the material is disposed of by high dilution with biotreatment, acid neutralization, deep well injection, incineration, wet air/catalytic/Humid Peroxide Oxidation or other specialty processes [2]. The two basic methods for treating spent caustic solutions are wet air oxidation (WAO) and direct acid neutralization (DAN), respectively. But these methods are not efficient, Because of high acid consumption and large caustic waste to effluent. In this new process the spent caustic are refined and toxic materials are removed and two valuable products namely NaOH and Na_2CO_3 are produced with high purity by an economical process [3].

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II. ENVIROMENTAL PROBLEMS

Each spent caustics including mercaptides or sulphides may be oxidized before neutralization to minimize COD of the final wastewater brine and sulfur amount of the neutralizer off gas. The control of pH in the neutralization stage is critical because the metallurgy is not designed for low pH operation (below 6). It is also important to minimize the production of gases such as H2S from any remaining Na2S and CO, from the sodium carbonate. Any mercaptans released in the neutralizer will also result in a highly odorous brine solution [5]. Spent Caustic is very toxic and highly odorous wastewater. The list below shows typical analytical results [6].

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1. Chemical Oxygen Demand (COD): 10,000 to 100,000 (mg/L).
2. Biochemical Oxygen Demand (BOD): 5,000 to 50,000 (mg/L).
3. Total Organic Carbon (TOC): 1,000 to 5,000 (mg/L).
4. Sulfides: 5,000 to 35,000 (mg/L).
5. High pH value.

Table 1.Permissible limit of Environmental Indicators.

Environmental Indicators	Permissible Limit (mg/L)
BOD	80-1600
COD	200-4000
TOC	80-260
Sulphide as H_2S	3

III. PRODUCT USAGES

Nowadays Caustic Soda and Sodium Carbonate are widely used in several industries:
Sodium hydroxide is a popular strong base used in industry. Around 56% of sodium hydroxide produced is used by industry, 25% of which is used in the paper industry.
Sodium hydroxide is also used in the manufacture of sodium salts and detergents, pH regulation, and organic synthesis. It is used in the Bayer process of aluminium production.
It is desirable to increase the alkalinity of a mixture, or to neutralize acids.

- Chemical pulping
- Tissue digestion
- Dissolving amphoteric metals and compounds
- Esterification and transesterification reagent
- Food preparation
- Cleaning agent
- Water treatment
- In cement mixers, mortars, concrete, grouts

IV. EXPLANATIONOF THE PROCESS

In this project because of essential need of the industrial units to restore spent caustic following benefits are:
1- The ability to remove hazardous compounds from wastewater.
2. Hazardous sodium sulfide (Na2S) removal in wastewater.
3. The production of a valuable substance such as NaOH and sodium carbonate rather than neutralizing it by acid or drop it in water due to high pH that is very harmful for environment.
The use of a new and modern technology compared to other technologies with more advantages.
1. Storage of wastewater in reservoirs and separation of fats or oils.
2. Advanced oxidation (AO) of wastewater.
3. Separating of disulfide oil compounds.
4. Filtration process.
5. Concentration stage.
Advanced oxidation (AO) of wastewater, is performed by wet air, ozone molecule, UV ray and appropriate catalyst.

A) Innovation of the Plan

1. Elimination of toxic materials from wastewater.
2- pH reduction and neutralization with lower cost.
3- Production of new product from effluent.
4- Use of cheap feed (wastewater) and low cost additives.
5- Benefit from energy optimization and exergy.
6- Utilization of new technology with high value added.
7- Purification of hazardous wastewater without any environmental risk.
8- Protection from environmental effects with high alkalinity property.

B) Pre-treatment Process

The pretreated spent caustic is filtered through 5 µm media upstream of the WAO reactor for removal of suspended polymers down to a hydrocarbon content of 10 ppm (wt). The oil and grease content of 146 ppm(wt) was largely a result of the polymer formation of the dienes left in the raffinate feed.

C) Storing and Advanced Oxidation (Initial Stage)

Upstream of the Pretreat unit, the spent caustic from the caustic tower is deoiled to remove the polymeric material formed in the spent caustic. It is then degassed by flashing part of the dissolved hydrocarbon gases. The spent caustic is then stored in a spent-caustic tank where oil and polymers float and are skimmed off from the spent caustic.

Advanced oxidation (AO) will oxidize all decreased sulfur materials and phenols, remove the foaming tendency of the spent caustic, and decrease a majority of the COD producing a biodegradable wastewater. AO is the best applied to refinery spent caustics used for treating heavy products and containing naphthenic constituents. AO can also be used to treat mixed spent caustics that may contain naphthenic as well as cresylic and sulfidic constituents. Type of spent caustic can determine the best treatment technique. AO found to be the most common treatment method to treat all type of spent caustics. Safety factor plays a major role in spent caustic treatment. The oxidation contactors exceeded its design values in two ways. The NA2S content in the oxidized product is less than 1 ppm(wt). The design guaranteed 5 ppm(wt). • There was a 97% conversion of NA2S to NA2SO4 in the oxidized product. The design guaranteed 90%.Thus, pretreat enhances the oxidation process, resulting in more efficient oxidation (better conversion of NA2S to NA2SO4) and potential elimination of a secondary oxidation step.

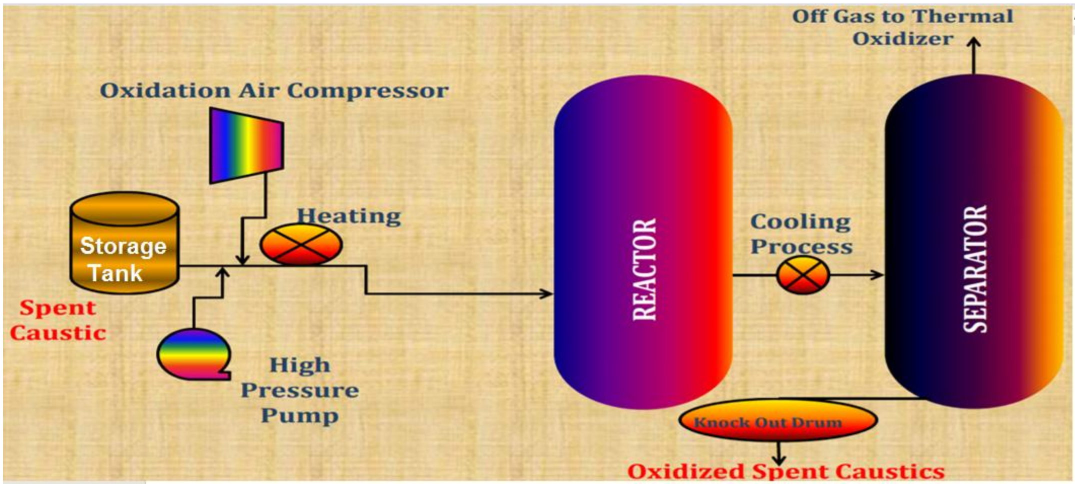

Fig 1. Schematic view of the storage and oxidation process.

After oxidation and conversion of components, some off gases are going out from the tanks. Also after (AO), some oils and polymers are separated by decantation and the remains of effluent enters reboiler to heat up liquid waste mixture and by means of crystallizer, the solid powders of product with this useful process, the NaOH or Na_2CO_3 are produced selectively. Schematic Map of Process is shown in the figure 2.

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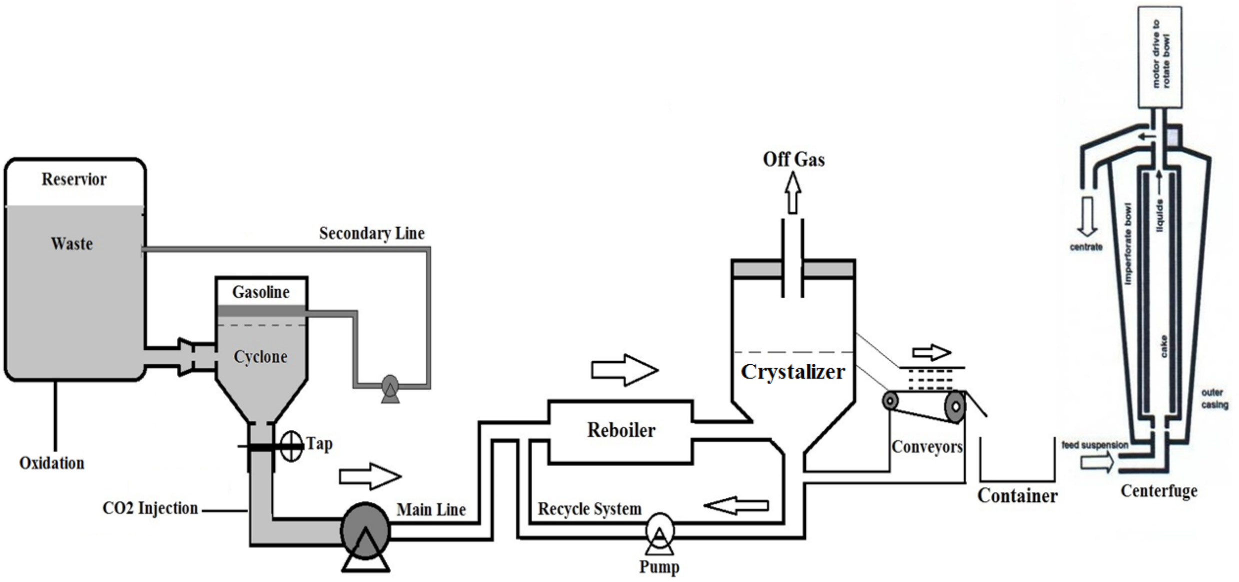

Fig 2. Schematic map of the treatment process.

V. INCREASING PURITYOFTHE PRODUCTS

After production of NaOH and Na2CO3 as solid powder, can be increase the product purity by some useful ways such as membrane and centrifuge system.

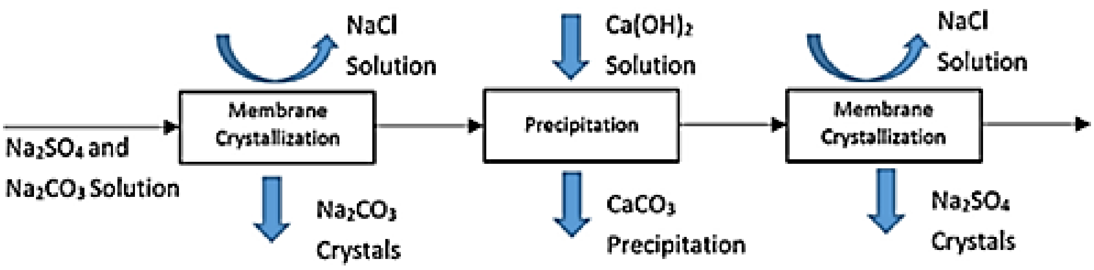

Fig 3. The Proposed scheme for Na2So4-Na2CO3 recovery by membrane crystallization.

VI. EXPERIMENT PROCESS

Some of wastewater is oxidized by wet air in 95-100 centigrade to convert toxic sulfide to sulfate and mercaptan to desulfate. After that, is heated to vaporize. After a while, about 75 percent of the effluent is vaporized and Na2CO3 crystal particles are produced. This procedure takes about 30 minutes.

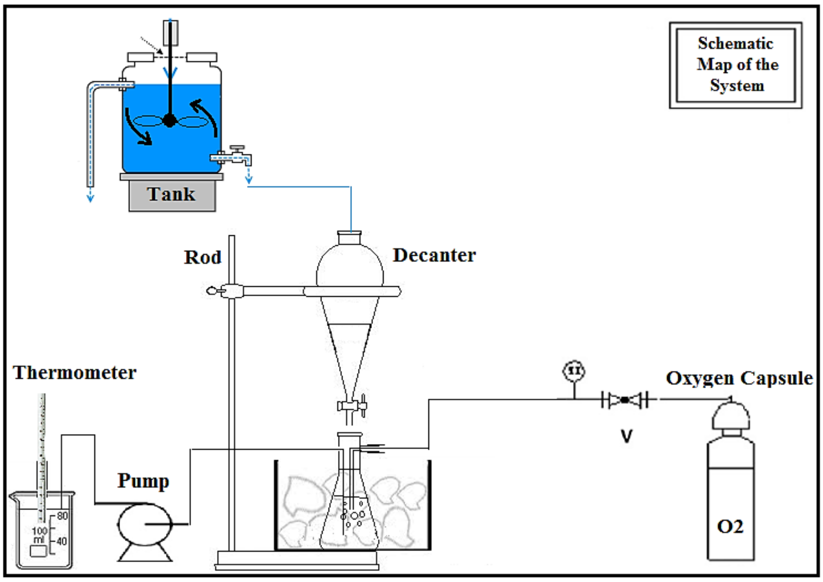

Fig 4. Schematic picture of the experimental setup.

VII. RESULTSAND DISCUSSION

The spent caustic generated in ethylene plants can be used in pulp and paper mills as makeup alkali in the Kraft recovery process. The hazardous nature of aromatic hydrocarbons, polymers, and polymer precursors, however, tends to inhibit this practice.

By reducing the quantity of hydrocarbons, polymers, and polymer precursors to less than 10 ppm in the spent caustic, the Pretreat process makes spent caustic attractive for use in pulp and paper mills. Pretreat converts a hazardous waste in the ethylene plants to a valuable by-product.

Other similar uses of pretreated spent caustic are found in noble metal catalyst manufacture, metal treatment processes, and leather tanning. The large number of pulp and paper units throughout the world (5,700 total) offer underutilized opportunities for economic and environmentally responsible disposal of spent caustic from the ethylene unit.

VIII. CONCLUSION

Advanced oxidation will oxidize all decreased sulfur materials and phenols, remove the foaming tendency of the spent caustic, and decrease a majority of the COD producing a biodegradable wastewater. AO is the best applied to refinery spent caustics used for treating heavy products and containing naphthenic constituents. AO can also be used to treat mixed spent caustics that may contain naphthenic as well as cresylic and sulfidic constituents. Type of spent caustic can determine the best treatment technique. AO found to be the most common treatment method to treat all type of spent caustics. Safety factor plays a major role in spent caustic treatment. Also after AO by means of useful process, the NaOH and Na2CO3 are produced.

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