A Study of Biological treatment of Spent Sulfidic Caustic

Amir Heidarinasab and Sayed Reza Hashemi

Abstract—Spent Sulfidic Caustic is a waste from Refineries and petrochemical plants which is difficult to treat and dispose of due to its noxious properties such as sulfides and mercaptans. Spent caustic has high chemical oxygen demand (COD) and this is not accepted in waste water treatment out fall. There are different ways to handling spent caustic. Neutralization of produced spent caustic is done in a separate plant usually through oxidation in most of the refineries. That is also possible to provide spent caustic to the pulp and paper mill industry depending upon the situation. Wet air oxidation (WAO) is considered to be a reliable technique for disposal of spent caustic but high investment makes a disadvantage to use this method. Biological treatment of spent caustic is the other way to complete oxidation of both inorganic and organic sulfur to sulfate and consequently to reduce COD. As investment for construction, operation and maintenance is dramatically lower than other methods this type of treatment seems to be more efficient. In this review we introduce few treatments which are already known for spent caustic treatment and then we discuss more about Biotreatment of spent caustic thioparus as new species recently used in Biotreatment of spent sulfidic caustic.

Keywords— Biological treatment, Chemical Oxygen demand, spent caustic, Waste water, Thiobacillus sp.

I. INTRODUCTION

Sodium hydroxide (NaOH) solutions are used in petroleum refining to remove hydrogen sulfide (H₂S) or Mercaptans(R-SH) from various hydrocarbon streams. Once mercaptan reacts with the majority of NaOH, the solution becomes known as a spent caustic. Spent Sulfidic Caustic can be classified into Phenolic or sulfidic, depending on their Phenolic and free NaOH content. They can vary from 240 g of Phenolic/L, 2 to 25 g of sulfides/L, 5 to 30 g of mercaptans/L and 5 to 18% free NaOH, Ammonia, cyanide, together with mono and polyaromatic nitrogen and sulfur compounds can also be found. Spent caustic characteristics can greatly vary from refinery to refinery. [1, 2]. It is possible to find trace of special catalysts as well. Spent caustics typically have a pH >12 and sulfide concentrations exceeding 2-3 wt%. Depending on the source, Spent caustic may also contain phenols, mercaptans, amines, and other organic compounds that are soluble or emulsified in the caustic [3]. Main chemical reactions in the process includes extraction and regeneration are:

The reaction of mercaptans with sodium hydroxide to form sodium mercaptide

\[ RSH + NaOH \rightarrow RSNa + H_2O \]

The Oxidation of the sodium mercaptides to form the disulphides plus sodium hydroxide

\[ RSNa + 1/4 O_2 + 1/2 H_2O \rightarrow RSSR + NaOH \]

As the spent caustic alkalinity is reduced, so also is its capacity to extract mercaptans. When disulfides accumulate to a few milligrams per liter, the OH⁻ content drops below 5% so a fraction of the solution is regularly purged off and renewed. Other causes of spending are the accumulation of mercaptans, Na₂S, Phenolic compounds, emulsified naphthenates, thiosulfate, carbonate and Fe^{2+} precipitates. Spent Caustics are most difficult of all industrial waste to dispose properly. In this paper first we introduce common of spent caustic neutralization methods and then we discuss about biological treatment for spent caustic.

II. NEUTRALIZATION OF SPENT CAUSTIC

There are several issues with the treatment of spent caustic streams:

- Sulfides and mercaptans have very strong odors. The odor thresholds for these types of compounds are generally in the order of magnitude of parts per billion. In addition, per OSHA, these compounds are considered very toxic and can be potentially hazardous to plant personnel. This is particularly true in processes where the spent caustic is acid neutralized, which causes hydrogen sulfide and mercaptan gases to be released.

- High concentrations of phenols in the spent caustic wastewater can cause issues in biological treatment processes. Phenol in concentrations as low as 400 mg/L have been shown to inhibit the removal of COD, ammonia and phosphorous as well as negatively impact the settling characteristics of the sludge. It should be noted that in many refineries, the production of spent caustics containing cresylic acids is performed as a batch process. This can cause periodic discharges of phenols and cresols to the wastewater treatment plant. It has been reported that sudden discharges of waste containing high concentration of phenols have caused complete inhibition of the biological treatment system.

- The spent caustic streams often contain a variety of compounds that are biorefractory.

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Literature reviews indicate that naphthenic acids have been shown to have limited biodegradation in conventional biological treatment processes.

- Naphthenic acids have foaming characteristics that can create issues when aerated or agitated during biological treatment.
- The untreated spent caustic streams are generally high in chemical oxygen demand (COD), in the range of 15 g/L to greater than 400 g/L. Depending on the volume of spent caustic that is present, this can result in a large COD load on downstream biological processes. Most of the companies neutralize their spent caustic through oxidation but some of them get rid of the spent caustic in a profitable way which is described below. The Shell Puget Sound Refinery in the United States cut off their waste disposal costs by providing their spent caustic to the pulp and paper mill industry in the northwest. Previously this spent caustic was transported to a waste facility about 2000 miles away from the plant site in Texas. The spent caustic is used in the pulp and paper mill’s Kraft process in green liquor. This new practice helped both industries to cut their costs about $400,000 per year [4]. Although this is the best recommendation but not applicable everywhere therefore neutralization is a must for this problematic waste stream to avoid environmental risks.

III. METHODS OF NEUTRALIZATION

A. Wet Air Oxidation

The Wet Air Oxidation (WAO) or hydrothermal treatment is a high temperature process for oxidation of materials that are suspended or dissolved in water with oxygen. Wet air oxidation system oxidizes sulphides and mercaptans to reduce COD of spent caustic. After treatment with WAO the effluent has a lower COD and can then be treated in the biological purification plant. In a typical WAO system, the feed is pumped to the system at a higher pressure (about 28 barg). The feed stream is mixed with compressed air and pre-heated with outgoing effluent from reactor in a heat exchanger. The hot fluid stream is then held in a reactor for one hour residence time at 200°C without any catalyst. The reactions take place in the liquid phase and the oxygen must be transferred to the liquid phase from the gas phase to carry out the reaction. Sulphide compounds oxidize partially to form thiosulphate, further oxidation gives sodium sulphate. The organic compounds present in the spent caustic are only partially oxidized. [2]

B. Chemical Reagent Oxidation

In this process, spent caustic is mixed with water-immiscible solvent (like pyrolysis gasoline) for extraction of polymerized hydrocarbons to avoid fouling in downstream equipments. The residence time is supplied to the mixture to get phase separation and thereafter the solvent phase is removed from the aqueous phase. The aqueous phase is then treated with air for oxidation in a process like WAO to reduce COD [5]

C. Catalytic Oxidation

In the process spent caustic is fed to an oxidizer with steam, air and carbondioxid. The oxidizer is a reactor with catalyst in the form of a fixed bed. The reaction takes place under mild conditions over the catalyst particles. After the reaction in the oxidizer excess air is separated from the aqueous stream. Sodium sulphides and bisulphides in the spent caustic are converted to sodium thiosulphates. Due to mild conditions only a small amount of sodium sulphate is formed. The treated solution has less COD, BOD and pH and can therefore be charged to the biological treatment plant without any harm. [6]

D. Pretreatment Technology

In this process the spent caustic is treated with hydrogenated gasoline in a liquid-liquid extractor. The treatment with gasoline is followed by steam stripping. Pretreat also improves the efficiency of oxidation processes if this caustic is treated further with WAO etc. [7]

E. Treatment with Regeneration

In this process spent caustic is oxidized with an air/ozone mixture at ambient temperature. The mixture contains 99% air and 1% ozone. The residence time in the reactor is 5 hours. After the oxidation in the reactor the solution is treated with ultraviolet radiation and passed through a micro- and nanofilter in series. The filtrate from the nanofilter is regenerated with caustic solution which is recycled back to the caustic solution tank [8]

F. Biological Treatment

A new process for biological treatment of spent caustic has been developed. Oxidation of sulphidic caustic is done in an aerobic reactor containing sulphide oxidizing bacteria. The sulphides present in the spent caustic are converted partially to sulphate and elemental sulphur. Sulphides and mercaptans in spent caustic are biologically treated. The conversion to elemental Sulphur and sulphates are obtained by controlling the redox potential of the bacterial medium. [9]

IV. BIOLOGICAL TREATMENT OF SPENT SULFIDIC CAUSTIC

Although biological treatment can be an inexpensive disposal option, many refineries do not have the waste water treatment capacity to treat the entire amount of spent caustic generated. Additionally, concerns regarding odors and toxicity frequently prohibit on-site treatment. Currently, most spent caustic generated by refineries are either sent off-site to commercial operation for recovery or reuse (e.g. pulp and paper mills) or for disposal by deep-well injection. Future regulatory changes could result in more stringent controls and increased cost for off-site management of spent caustic. In such an event, low cost, on-site treatment options would be desired. Even without regulatory changes, current off-site transportation and disposal costs warrant future investigation of on-site management alternatives. Wet air oxidation for on-
site management is commercially available, but can result in significant capital investment and high operation costs. Wet air oxidation can be particularly expensive for spent caustic streams from small to medium size refineries owing to an insufficient economy of scale. [13]

Thiobacillus sp. is widely used in studies of the conversion of H2S and other sulfur compounds by biological processes [14]. These bacteria have the ability to grow under various environmental stress conditions such as oxygen deficiency, acid conditions, etc. Many Thiobacillus sp. have acidophilic characteristics and are able to develop in condition of low pH between 1-6 [15] some other Thiobacillus sp. May develop in neutral medium at pH of 6-8. T. denitrificans and T. thioparus which are able to grow facultatively on reduced sulfur compounds by reducing nitrate (NO3-) to nitrogen gas [16]

Mercaptan-free, spent-sulfidic caustics from two refineries were successfully biotreated at the bench scale (1.5 L) and pilot scale (3.7 m3), resulting in neutralization and removal of active sulfides [10, 11]. Sulfides were completely oxidized to sulfate by T. denitrificans. But many refinery spent-sulfidic caustics also contain mercaptans. Although mixotrophic strains of certain Thiobacilli have been reported [12], T. denitrificans strain F is strictly autotrophic and incapable of using organic sulfur compounds as carbon and energy sources. Therefore, a microbial culture capable of oxidation of both inorganic sulfur and organic sulfur compounds, such as mercaptans, will be either mixotrophic or a co-culture of a heterotrophic organism capable of mercaptan oxidation and an autotrophic, sulfate-oxidizer such as T. denitrificans. [13]

The result of a typical Fluidized bed bioreactor is shown in table 1 when Thiobacillus sp. are used [21].

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<th>Table 1: Sulfur mass balance in FBR during 51 days of biological sulfide oxidation process using Thiobacillus sp.</th>
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**FBR**: fluidized bed bioreactor

Another species T. thioparus may be involved with the oxidation of both types of inorganic and organic sulfur in the volumetric productivity of the Biotreatment system was about fivefold higher than that observed previously in suspended culture but was limited by sulfate inhibition. The biological sulfide-removing studies employs either photautotrophic or chemolithotrophic. Sulfide-oxidizing bacteria (SOB). Bioreactors employing chemotrophic SOB generally achieved higher sulfide loading rate than phototrophic systems. The simpler nutritional requirements and higher sulfide tolerance of chemotrophic organisms favored their application in biological sulfide oxidation systems. The bacteria involved in sulfide oxidation belong to a group of colorless sulfur bacteria, of which Thiobacillus is the best known. Thiobacillus is mostly facultative autotrophic, utilizing reduced inorganic sulfur compounds as electron donors and carbon dioxide as a carbon source. However, some heterotrophic Thiobacilli were reported in a sulfide-oxidizing reactor, when the sulfide laden wastewater contained organic matter [17-20] under the present circumstances, sulfide oxidation using biotechnological methods is the best suitable alternative. Organisms belonging to the group of colorless sulfur bacteria oxidize sulfide to elemental sulfur under circumstances of oxygen-limiting conditions. Based on this feature, many researchers worked for biological oxidation using various types of microorganisms [19, 20].

As seen in Fig.1, the sulfate concentration in the system reached a steady state of about 97 mM after 600-700 h of operation. Based on the caustic analysis in the predicted steady-state concentration was 92 mM. Therefore, complete oxidation of both inorganic and MeSH sulfur to sulfate is indicated. [13]

![Fig.1 Sulfate concentration in the caustic biotreatment system continuous operating](image)

### V. Conclusion

Neutralization of produced spent caustic is done in a separate plant usually through oxidation in most of the refineries. Wet air oxidation for on-site management is commercially available, but can result in significant capital investment and high operation costs. Removal of sulfide from the industrial waste streams is presently being done by chemical methods, which are expensive as well as environmentally not benign. Biological treatment of spent caustic is the other way to complete oxidation of both inorganic and organic sulfur to sulfate and consequently to reduce COD. And due to above description using biological treatment could be reliable and economical method.

T. denitrificans strain F is strictly autotrophic and incapable
of using organic sulfur compounds as carbon and energy sources. *T. thioparus* also may be involved with the oxidation of both types of inorganic and organic sulfur. To know which one could be more effective, future tests and laboratory results will show that in the same sample and will be issued in next lecture.

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