



# A comparative study of the treatment of ethylene plant spent caustic by neutralization and classical and advanced oxidation



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## ABSTRACT

The treatment of spent caustic produced from an ethylene plant was investigated. In the case of neutralization alone it was found that the maximum removal of sulfide was at pH values below 5.5. The higher percentage removal of sulfides (99% at pH = 1.5) was accompanied with the highest COD removal (88%). For classical oxidation using H<sub>2</sub>O<sub>2</sub> the maximum COD removal percentage reached 89% at pH = 2.5 and at a hydrogen peroxide concentration of 19 mM/L. For the advanced oxidation using Fenton's process it was found that the maximum COD removal of 96.5% was achieved at a hydrogen peroxide/ferrous sulfate ratio of (7:1).

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## 1. Introduction

Sodium hydroxide solutions are used in many chemical industries (i.e. liquefied petroleum gas, natural gas, and refining industries) to wash out different gases such as hydrogen sulfide and carbon dioxide from different hydrocarbon streams (Hashemi and Heidarinasab, 2012). Once these gases react with sodium hydroxide a waste solution known as spent caustic will be produced (Hashemi and Heidarinasab, 2012). Spent caustic is considered to be one of the liquid industrial wastes that are not easy to handle and to dispose of, due to its high content of pollutants, alkalinity (pH > 12), high salinity (sodium of 5–12 wt%) and high sulfide concentration (2–3 wt%) (Kumfer et al., 2010; Alnaizy, 2008; Olmos, 2004; Sheu and Weng, 2001). Accordingly, special management of spent caustic is required where treatment of spent caustic before it could be sent to a conventional wastewater treatment plant is a must.

Depending on which industry is producing the spent caustic and on the source of fuel that the fresh caustic is washing, spent caustic can be classified into three main types. Table 1 summarizes the

three main types of spent caustic and their main characteristics. Usually refineries do not separate each type of spent caustic and they mix the three types, this is referred to as the mixed refinery spent caustic (Alnaizy, 2008). Numerous efforts have been made to develop and to enhance the treatment process of spent caustic. Treatment methods for spent caustic can be classified into three main categories: biological, chemical and thermal processes (Ahmad, 2010). Every category has its own advantages and disadvantages. Among the three mentioned categories chemical treatment processes are considered to be the most common. Chemical oxidation can be classified into two categories: classical chemical oxidation and advanced chemical oxidation processes (AOPs). In the classical chemical oxidation process a chemical oxidant is directly added to the waste stream in order to oxidize any available contaminants. The most commonly used chemical oxidants are: chlorine, chlorine dioxide, oxygen, persulfate, permanganate, ozone, and hydrogen peroxide. Table 2 summarizes the main advantages and disadvantages of each oxidant.

Advanced chemical oxidation processes (AOPs) are considered to be promising methods for the treatment of spent caustic. AOPs would form sufficient quantities of highly reactive hydroxyl radicals (HO•) at near ambient temperature and pressure in order to attack complex chemical contaminants in the waste stream (Munter,

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**Table 1**  
Different spent caustic types and their characteristics.

Type of spent caustic	Sulfidic	Cresylic	Naphthenic	Ref.
Source	Ethylene and Liquefied Petroleum Gas (LPG)	Gasoline	Kerosene and Diesel	(Kumfer et al., 2010)
Content	High concentration of sulfides and mercaptans	High concentration of phenols & cresols	High concentration of polycyclic aliphatic organic compounds	(Kumfer et al., 2010)
Chemical Oxygen Demand (COD) (ppm)	5000–90,000	50,000–100,000	150,000–240,000	(Ahmad, 2010)
Total Organic Carbon (TOC) (ppm)	20–3000	10,000–24,000	24,000–60,000	(Ahmad, 2010)
Sulfides (ppm)	2000–52,000	<1	0–63,000	(Ahmad, 2010)
Total phenol (ppm)	2–30	1900–1000	14,000–19,000	(Ahmad, 2010)

2001). AOPs could reduce the concentration of certain pollutants in spent caustic to a very low concentration below 5 ppb (Canizares et al., 2009). In order to achieve the required level of treatment AOPs are usually paired with other treatment systems. In such cases the treatment process will be more complex and more costly. A large number of methods are classified as AOPs. The generation of the hydroxyl radicals are achieved by the use of one or more strong oxidants (e.g.  $H_2O_2$ ,  $O_2$ , and  $O_3$ ) and/or catalysts (e.g. titanium dioxide, transition metal ions) and/or energy sources (e.g. ultraviolet radiation) (Munter, 2001). The selection of a certain advanced oxidation process depends on the type of compounds to be removed, treatment objectives, concentrations of pollutants, site considerations, and cost. The main processes found in literature for producing the required radicals are summarized in Table 3.

It can be noted from Table 3 that the UV system has major drawbacks such as mass transfer limitations and turbidity and other compounds (i.e. nitrate) interference with UV light which will result in lowering the process efficiency. The ozone/hydrogen peroxide system is similar to UV/hydrogen peroxide system in many ways. However, the ozone/hydrogen peroxide system is less affected by the feed characteristics. The combination of ozone, hydrogen peroxide, and ultraviolet radiation ( $O_3/H_2O_2/UV$ ) in one system will enhance the treatment process. However, in this case the cost of treatment will be high.

As mentioned before spent caustic solutions generated from petroleum refineries and/or from petrochemical industries vary highly in quantity and quality. These depend on the type of processed material, the different operational units, and the different operational conditions. In this study spent caustic produced from an ethylene plant was targeted. Ethylene is produced from an ethane rich gas (ERG) which is supplied from Qatar petroleum refinery. None of the previous studies compared the treatment of spent caustic produced from an ethylene plant by several chemical processes namely, neutralization, neutralization coupled with classical oxidation, neutralization coupled with advance oxidation. The targeted COD and sulfide concentrations were 1000 mg/L and 2 mg/L, respectively. At these concentrations the treated spent caustic can be handled by conventional biological treatment. The effect of different parameters on the treatment process was investigated namely, pH, oxidants concentration and the ratio of oxidant concentration to catalyst concentration.

## 2. Materials and methods

### 2.1. Characterization of spent caustic

Spent caustic is a dark brown to black solution its composition is highly variable depending on the type of petrochemical industry it is produced from. Samples of spent caustic were collected from Qatar Petrochemical Company (QAPCO). QAPCO is a petrochemical company in Qatar that produces ethylene and polyethylene for the plastic industry. Three samples were collected from QAPCO's petrochemical plant at three different times. After collection samples were stored in a refrigerator at 4 °C until use. Each test was done in triplicate. The main characteristics of the collected samples are summarized in Table 4. In Table 4 the range (min. value – max. value) of the analyzed samples is presented.

Comparing the results in Table 4 with other refinery spent caustic solution it was found that ethylene spent caustic has a relatively low COD and BOD concentrations. Where the COD and BOD concentrations for other refinery spent caustic solutions range between (20,000–50,000 ppm) and (5000–15,000 ppm), respectively. Moreover, sulfide and phenol concentrations are also relatively lower than other refinery spent caustic. Where the sulfide and phenol concentrations for other refinery spent caustic solutions range between (0–64,000 ppm) and (0–20,000 ppm), respectively. The different characteristics of such spent caustic is expected to highly affect the treatment process.

### 2.2. Experimental procedure

Neutralization and Oxidation experiments were performed in a batch system with different reagents concentrations. The experimental apparatus used in the batch tests consisted of a magnetically stirred round bottom pyrex glass flask (250 ml), 25 ml burettes were used to add the required reagents, and temperature was controlled by a magnetic stirrer hot plate (Stuart Scientific, UK). Temperature and pH were continuously measured using a pH/ORP meter (HANNA Instruments, HI 2211). In order to ensure homogeneous conditions in the reactor the solution was continuously mixed at a speed of 100 rpm. The degree of stirring was kept mild as any excessive stirring lead to excessive foaming. Sulfuric acid 98% (v/v) (panreac) and 5.0 M sodium hydroxide solutions were used for pH control. Lab grade hydrogen peroxide at the concentration of 30% (v/v) (panreac) was used as the oxidant reagent and ferrous sulfate (heptahydrated) was used as the catalyst. The advanced oxidation process was implemented by adding ferrous sulfate catalyst (6.6 mM/L), then hydrogen peroxide (20 mM/L) was dosed into the reactor. After 60 min of reaction time samples were withdrawn from the reactor, neutralized to a pH value around 7.0, centrifuged to separate the iron floc at a speed of 2000 rpm using a Centurion Scientific centrifuge (K3 series) and then samples were decanted and analyzed for COD and sulfide concentrations.

## 3. Results and discussion

### 3.1. Neutralization

Fig. 1 shows the impact of pH value on the sulfide and COD removal. From Fig. 1 it could be seen that as pH value decreases the percentage removal for both sulfides and COD increases. The reason behind the increase of sulfides removal at low pH values is that sulfides exist in three different forms  $H_2S$ ,  $HS^-$ ,  $S^{2-}$  depending on the pH value as shown in reactions (1) and (2):

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