



Semnan University

# Progress in Engineering Thermodynamics and Kinetics Journal

Journal homepage: <https://jpetk.semnan.ac.ir/>

## Research Article

# Optimization of Spent Caustic neutralization of South Pars gas refinery using sulfuric acid method

Ziba Mohammadizadeh<sup>a</sup>, Amir Farshi<sup>b\*</sup>, Naeimeh Jodeiri<sup>c</sup>, Sayed Javid Royaee<sup>d</sup>

<sup>a</sup> M.Sc. in Chemical Engineering, Sahand University of Technology

<sup>b</sup> Assistant Professor of Chemical Engineering, Research Institute of Petroleum Industry

<sup>c</sup> Assistant Professor of Chemical Engineering, Sahand University of Technology

<sup>d</sup> Associate Professor of Chemical Engineering, Research Institute of Petroleum Industry

## ARTICLE INFO

### Article history:

Received: 202\*\_\*\*\_\*\*

Revised: 202\*\_\*\*\_\*\*

Accepted: 202\*\_\*\*\_\*\*

### Keywords:

Spent caustic;  
Neutralization;  
South Pars gas refinery;  
Sulfuric acid;  
COD reduction.

## ABSTRACT

Spent caustic is one of the most hazardous byproducts of oil refineries, gas processing, and petrochemical industrial processes. In this study, Central Composite Design (CCD) was employed to optimize the neutralization process. Experimental data were analyzed via Design Expert software, identifying initial temperature and reaction time as the critical parameters. The Chemical Oxygen Demand (COD) reduction was modeled as a linear equation. Results indicate that using the sulfuric acid neutralization method for spent caustic treatment, the COD was reduced from a high value of 34,000 ppm to 8,000 ppm. All sources of harmful components of the spent caustic were converted into stable sulfate salts. The industrial discharge limit for spent caustic wastewater requires a COD value in the range of 60-100 ppm. However, this target is difficult to achieve directly and is typically attained by diluting the treated effluent. Monitoring revealed a correlation between pH and COD levels: as the pH dropped from 14 to 12 (free caustic neutralization), then to 7, and finally to 2, the COD decreased from 34,400 ppm to approximately 20,000 ppm, and ultimately to 8,000 ppm, respectively.

© 2025. Progress in Engineering Thermodynamics and Kinetics Journal published by Semnan University Press.

## 1. Introduction

Spent caustic is a hazardous byproduct generated in oil refineries and natural gas processing plants. It is characterized by a foul odor and severe corrosivity due to the presence of sulfide salts, mercaptans, and organic materials such as disulfides. Due to its high alkalinity, toxicity,

\* Corresponding author.

E-mail address: [farshia@ripi.ir](mailto:farshia@ripi.ir)

### Cite this article as:

Mohammadizadeh, Z., Farshi, A., Jodeiri N., Royaee S.J. (2025). Optimization of spent caustic neutralization of south Pars gas refinery using sulfuric acid method. *Progress in Engineering Thermodynamics and Kinetics*, 1. (3.), pp. 299-315.

<https://doi.org/10.22075/jpetk.2025.36325.1022>

and high chemical oxygen demand (COD), environmental regulations strictly prohibit its direct discharge. Consequently, effective treatment to remove toxic substances and reduce COD is mandatory. The COD value for sulfidic spent caustic of South Pars Gas Refinery is 34,400 ppm. The presence of mercaptans in light/heavy petroleum products and natural gas causes fresh caustic to be converted to spent caustic during the demercaptanization process of petroleum products, since the caustic solution is used to remove mercaptan and other undesirable compounds from petroleum refining streams [1, 2]. After removing the mercaptans from hydrocarbons stream, the caustic solution is converted into spent caustic [2, 3]. Spent caustic is subsequently sent to the regeneration unit, where it is treated until partial recovery of the caustic solution is achieved. As the caustic solution continuously circulates within the absorption–regeneration loop, the accumulation of salts and impurities gradually degrades its quality. Consequently, to maintain the desired caustic concentration and process efficiency, a portion of the circulating solution must be periodically drained. This drained stream is referred to as spent caustic [4]. In addition to refinery operations, several other industries, including LPG processing and natural gas (methane) treatment units, also generate significant quantities of spent caustic. One of the most hazardous substances associated with spent caustic during neutralization with sulfuric acid is hydrogen sulfide, which is extremely toxic, potentially lethal, and characterized by a strong and unpleasant odor. Owing to the presence of harmful impurities and its high chemical oxygen demand (COD), direct discharge of spent caustic into the environment is not permitted. For environmental disposal, the COD value of treated spent caustic must be reduced to approximately 60 ppm [2].

Spent caustic streams are categorized into three types: sulfidic, cresylic, and naphthenic [2, 3]. Sulfidic spent caustic contains sulfur (0.5–4%) and mercaptans (0.1–4%); naphthenic spent caustic contains naphthenic acids (up to 15% in diesel) and a low amount of sulfide; however, cresylic spent caustic is rich in phenols, cresols, and organic acids [5]. Owing to its high alkalinity, salinity, elevated levels of sulfide, and the presence of toxic sulfur compounds such as methyl mercaptan (methanethiol), as well as aromatic hydrocarbons such as benzene, spent caustic is considered highly hazardous to the environment and therefore must be properly treated before discharge [6].

Methods for spent caustic treatment include deep well injections, incineration, wet air oxidation (WAO), advanced oxidation, biological treatment, catalytic oxidation, coagulation, and neutralization [2, 7].

Hawari et al. [3] investigated the treatment of ethylene plant spent caustic of Qatar Petrochemical Company. They compared three methods: acid neutralization, classical

oxidation, and advanced oxidation. In the neutralization method, a higher percentage of removal of sulfide (99%) at pH=1.5, with the highest percentage of COD removal (88%) was achieved. In the classical oxidation process, a maximum COD removal efficiency of 89% was obtained at pH = 2.5 and a hydrogen peroxide concentration of 19 mM L<sup>-1</sup>. Further increases in hydrogen peroxide concentration led to a decline in COD removal, suggesting scavenging effects and the existence of an optimal oxidant concentration. In contrast, the advanced oxidation process achieved a maximum COD removal of 96.4% at pH = 2.5 with a hydrogen peroxide to iron sulfate molar ratio of 7:1. Accordingly, advanced oxidation demonstrated the highest overall COD removal efficiency (approximately 96%).

De Graaff M. et al. [6] studied the biological treatment of spent caustic and found that a two-step process was better than a one-step process due to the high removal rate of sulfur, and the total volume of the reactor in the two-step process (VR1 + VR2) is 22% less than the reactor volume of a one-step process.

Farzi et al. [7] investigated the neutralization of spent caustic generated by the Tabriz petrochemical complex using sulfuric acid. They concluded that the proposed method is cost-effective and exhibits a favorable reaction rate under moderate temperature and atmospheric pressure conditions. The process also produces valuable by-products such as sodium sulfate, with the optimum operating conditions reported as 45 °C and a reaction time of 2 min. Their results further showed that color and phenol contents were significantly reduced within 30 min, and that the initial temperature had a pronounced effect on the treatment efficiency.

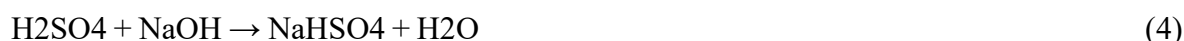
Gameel A. et al. [8] applied the electro-Fenton process for the treatment of spent caustic generated by the Sidi Karir petrochemical company in Alexandria, Egypt, using iron and stainless-steel electrodes. They reported that current density, H<sub>2</sub>O<sub>2</sub> concentration, reaction time, initial pH, and the mode of H<sub>2</sub>O<sub>2</sub> addition are key parameters influencing the treatment efficiency. COD removal increased with increasing current density and hydrogen peroxide concentration up to an optimum level, beyond which the efficiency decreased. The initial pH was identified as a critical parameter, with pH = 3 reported as the optimal value. Moreover, continuous addition of hydrogen peroxide was found to enhance COD removal efficiency.

Carlos T. et al. [9] employed wet air oxidation (WAO) for the treatment of refinery spent caustic and reported effective elimination of unpleasant odors associated with sulfide and mercaptan compounds. Following WAO, the treated effluent was discharged to a biological treatment unit for further processing. However, despite its effectiveness, the industrial application of the WAO process remains limited due to its high capital investment requirements and hazardous operating conditions.

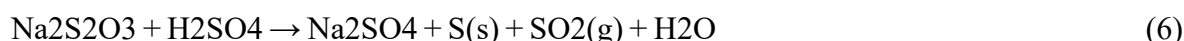
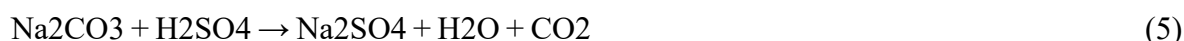
The main finding of the paper is that using the sulfuric acid neutralization method for spent caustic treatment, the COD of the spent caustic was reduced from a high value of 34,000 ppm to 8,000 ppm. During neutralization, the harmful components of spent caustic were converted into sulfate salts. Nevertheless, it should be noted that the industrial discharge limit for spent caustic wastewater typically requires COD values in the range of 60–100 ppm, indicating that neutralization alone is insufficient to meet discharge standards. Although the reaction between sulfuric acid and spent caustic is rapid and highly efficient, it is accompanied by vigorous gas evolution and heat release. Therefore, the neutralization process must be carried out slowly and with strict operational control to ensure safety. In addition, the reaction leads to the precipitation of sodium sulfate as a by-product. Consequently, sulfuric acid neutralization not only reduces the hazardous nature of spent caustic but also enables the recovery of a valuable industrial salt, namely sodium sulfate [7]. The reactions of spent caustic with sulfuric acid are as follows: by adding sulfuric acid to the caustic solution, sodium bisulfate and then sodium sulfate are formed:



As the molar quantity of sodium hydroxide in spent caustic solutions is greater than that of the acid, the addition of sulfuric acid to the caustic solution initially leads to the formation of sodium bisulfate. By adding more acid to the solution, sodium sulfate is subsequently formed according to reaction no. 4, which is analogous to reaction no. 1 involving an acid salt.



Therefore, reactions 3 and 4 are suitable for wastewater treatment because, for the production of sodium sulfate, two moles of caustic solution are required per mole of acid. According to the above clarification, it can be concluded that sodium sulfate is the reaction product, and if the solution is saturated with this salt, it will precipitate from the solution. In addition, sulfuric acid can react with existing sodium carbonate, sodium thiosulfate, and sodium sulfite to convert them to sodium sulfate according to the following reactions:



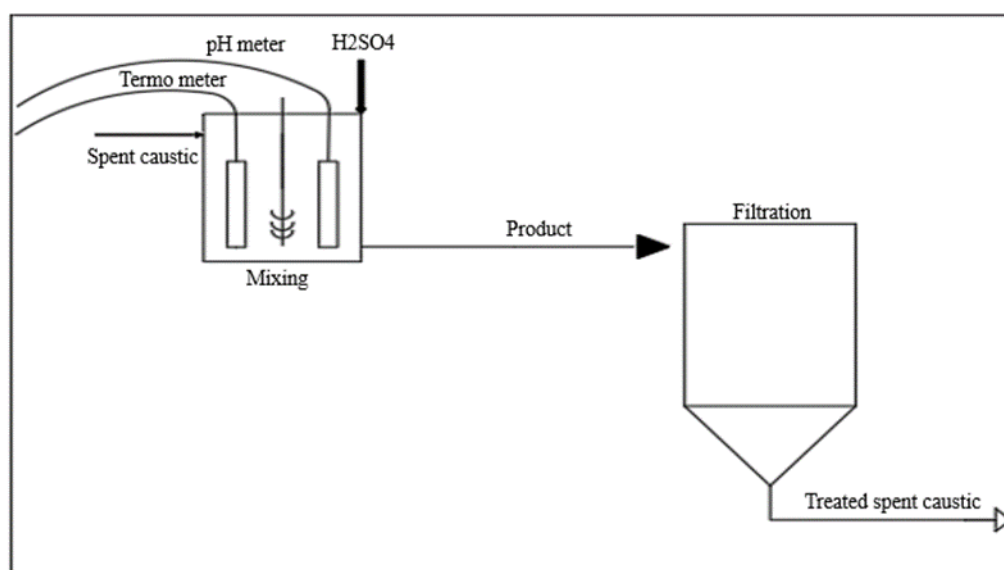
According to reaction number 7, sodium sulfide is converted to sodium sulfate and  $\text{H}_2\text{S}$ . The generation of  $\text{H}_2\text{S}$  is undesirable from health and corrosion viewpoints, as  $\text{H}_2\text{S}$  is toxic and adversely affects personnel health, and it also causes corrosion of reactors and auxiliary

equipment. According to the above reactions (no. 3 and 7), for 100 mL of spent caustic, the following amounts of sulfuric acid (density =  $1.84 \text{ g mL}^{-1}$ ) are required:

- 1- 5.03 mL, equal to 0.09444 g mol of sulfuric acid, for reaction no. 3
- 2- 0.31 mL, equal to 0.005820 g mol of sulfuric acid, for reaction no. 7.

## 2. Experimental Setup and Method[12]

All The experimental schematic for the present study is shown in Figure 1.



**Figure 1.** Experimental schematic diagram including the following steps: first step (left side of figure) (1) A glass mixing vessel with agitator and heater, second step (right side of figure) (2) a filtrated system with a vacuum pump.

Initially, 100 mL of spent caustic was added to a glass vessel, equivalent to 107.72 g, and stirred at 320 rpm. A pH meter was inserted into the beaker so that the pH of the solution could be continuously monitored. Sulfuric acid was added slowly. After acid addition, the temperature increased, and the system was allowed to stabilize between 0.5 and 2.5 minutes, depending on the test conditions. The feed was tested at three different temperatures (25, 35, and  $45^\circ\text{C}$ ) under atmospheric pressure. The titration process was continued until the pH reached 7. The temperature of the solution was measured using a thermometer. After completion of the reaction, the remaining solution was filtered using filter paper and a vacuum pump. The filtered solution was considered the treated product. A sample of the solution was sent to the laboratory for measurement of Chemical Oxygen Demand (COD).

The Chemical Oxygen Demand (COD) method determines the quantity of oxygen required to oxidize organic matter in a waste sample under specific conditions of oxidizing agent, temperature, and time. Chemically combined oxidants that enter natural water also undergo oxidation reactions. This type of reaction creates a chemical demand for oxygen, known as COD. As a result, the COD of sewage, wastewater, or contaminated water is defined as the amount of oxygen required to oxidize the oxidizable material contained therein. COD is typically measured using a strong oxidizing agent in an acidic environment. Pollutants that cannot be oxidized by oxygen may be oxidized by microorganisms, which is referred to as biological oxygen demand (BOD) [10].

### 3. MATERIALS AND METHODS

Spent caustic and sulfuric acid were used in this research. Spent caustic was obtained from phases 4 and 5 of Assaluyeh at the South Pars gas field of Iran. The specifications of anion and cation components and other chemical properties of spent caustic are presented in Table 1.

**Table 1:** Spent caustic chemical properties of South Pars gas refinery of phases 4 and 5 before and after neutralization treatment.

Specification	Before treatment(ppm)	After treatment(ppm)
COD	34400	6600
TDS	137230	15%
Chloride	113	240
TOC	Non extractable	-
Nitrite	<1	460
Nitrate	66	230
Sulfite	199	<230ppm
Sulfate	375	12%
Oxalate	<1	<1ppm
Phosphate	<1	<1ppm
Thiosulfate	152	<1ppm
Thiocyanate	22	<1ppm

In the same manner, a blank containing the reagents and a volume of distilled water equal to that of the sample was refluxed and titrated. Extreme care was exercised during this procedure because even trace amounts of organic matter on the glassware or from the atmosphere may cause significant errors. If higher sensitivity was required, a larger volume of sample was concentrated prior to digestion under reflux. All reagents were added to a sample larger than

50 mL, and the total volume was reduced to 150 mL by boiling in the refluxing flask open to the atmosphere without a condenser attached. The amount of H<sub>2</sub>SO<sub>4</sub> to be added (before concentration) was calculated based on a weight ratio of 10:1 (H<sub>2</sub>SO<sub>4</sub>:Cl<sup>-</sup>), using the chloride content of the original sample volume. A reagent blank was processed using the same procedure. This technique allows sample concentration without significant loss of easily digested volatile materials, although hard-to-digest volatile compounds such as volatile acids may be lost. The analytical method was validated using a standard potassium hydrogen phthalate solution [11].

$$\text{COD as mg O}_2/\text{L} = \frac{(A-B) \cdot M \cdot 8000}{\text{mL sample}} \quad (8)$$

#### 4. EXPERIMENTAL DESIGN METHOD

Experimental design methodology was used to optimize the number of laboratory tests. Among various design approaches, the Central Composite Design (CCD) method was selected. In statistics, a central composite design is an experimental design commonly applied in response surface methodology to construct a second-order (quadratic) model without the need for a full three-level factorial experiment.

After performing the designed experiments, linear regression analysis was applied to obtain the results. Coded variables were used in constructing the design. A Box–Wilson central composite design consists of an embedded factorial or fractional factorial design with center points, augmented by star points to estimate curvature. If the distance from the design center to a factorial point is  $\pm 1$  unit, the distance to a star point is  $|\alpha| > 1$ , where  $\alpha$  depends on the desired design properties and number of factors.

In this study, the CCD method was used for experimental design. Two factors were selected as input variables: reaction time and initial temperature. The ranges of the input variables are presented in Table 2 [12].

**Table 2.** Experimental design variable for laboratory tests.

Input variable	Range
Time mixing of reaction (min)	0.5-2.5
Temperature (°C)	25-45

The number of levels for mixing time is 0.5, 1.5, 2.5, and the number of levels for temperature is 25, 35, 45 (°C).

## 5. RESULTS AND DISCUSSION

The experimental design matrix and COD results obtained using the CCD method are presented in Table 3. The highlighted experiments indicate repeated runs. A quadratic model was used to analyze the experimental data [12].

**Table 3.** Design of laboratory data table according to the CCD method and the result of experimental data for COD.

Runs	Mixing Time of reaction (min)	Temperature (°C)	COD (ppm)
1	1.5	45	11500
2	2.5	25	8800
3	2.5	45	13000
4	2.5	35	9600
5	0.5	25	6600
6	1.5	35	9900
7	1.5	35	9400
8	1.5	25	8100
9	0.5	35	9200
10	1.5	35	10200
11	0.5	45	10400
12	1.5	35	8400

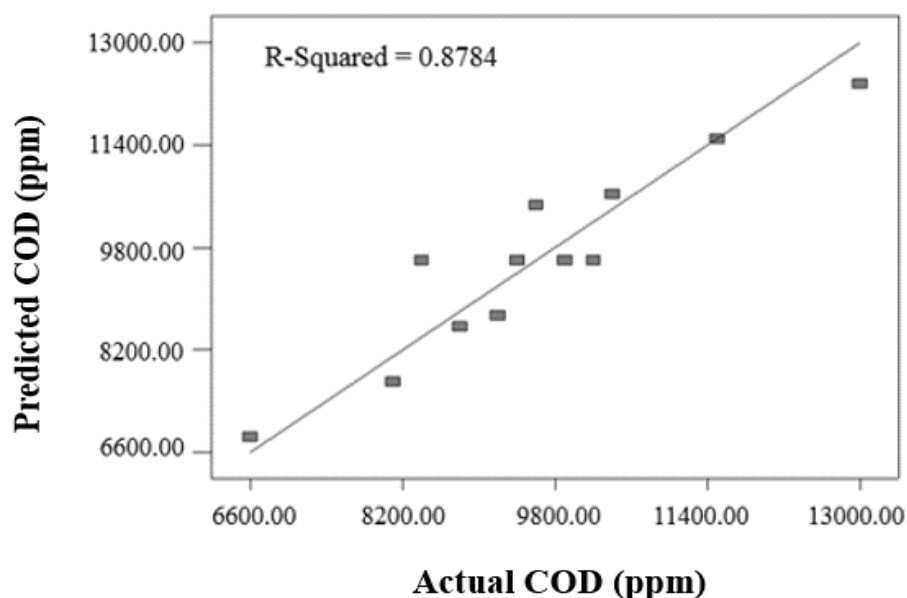
The analysis of variance (ANOVA) results are presented in Table 4.



**Table 4.** Analysis of variance of the experimental design experimental data table.

Source	Sum of Squares	df	Mean Square	F Value	p-value Probe>F	
Model	2.617E+007	2	1.308E+007	32.51	<0.0001	significant
A-T	2.166E+007	1	2.166E+007	53.81	<0.0001	
B-t	4.507E+006	1	4.507E+006	11.20	0.0086	
Residual	3.622E+006	9	4.025E+005			
Lack of fit	1.755E+006	6	2.925E+005	0.47	0.8020	not significant
Pure Error	1.868E+006	3	6.225E+005			
Cur Total	2.979E+007	11				

The F-value of the model indicates its statistical significance. The p-values of both factors are below 0.05, demonstrating that both variables significantly affect the process. The lack-of-fit term was not significant, confirming the adequacy of the model. Figure 2 compares the predicted and experimental COD values.


**Figure 2.** Predicted vs. Actual value of spent caustic COD is shown.

As shown in Figure 2, the R-squared value is close to unity, indicating good agreement between the model predictions and experimental data. The final equation for COD prediction is provided in Equation 9.

$$\text{COD} = +9561.67 + 1900.00 * \text{Temperature} + 866.67 * \text{Mixing Time} \quad (9)$$

Optimization results show that decreasing both the initial temperature and mixing time leads to a reduction in COD. At higher temperatures, the solubility of pollutants in spent caustic increases, resulting in less COD reduction. At lower temperatures, salt solubility decreases, leading to greater COD reduction. The optimum condition was obtained at 25 °C and a mixing time of 0.5 min, corresponding to a COD value of approximately 6600 ppm. The values of the acid–pH and acid–temperature as a function of sulfuric acid amount are depicted in Figure 3 and Figure 4, respectively, for the average interval test.

## 6. Impact of pH on Reaction Efficiency

The pH of spent caustic soda is about 14. The pH is reduced by adding sulfuric acid. Initially, the added acid is consumed in neutralizing the free caustic soda, and during this stage, the pH value does not change significantly. Once the free caustic soda is neutralized, the pH changes rapidly, and other components are neutralized accordingly. The substances present in spent caustic include carbonates, sulfides, and sulfates in various forms. During neutralization, starting from pH 14, the pH decreases to 12 and then rapidly reaches a neutral value of 7 when free NaOH is completely neutralized. With further acid addition, the pH decreases to approximately 2. The greatest COD reduction occurs at pH 2.

## 7. Monitoring pH Changes

The pH of spent caustic initially has a value of about 14. The pH changes due to the addition of sulfuric acid. A large initial amount of sulfuric acid is required to neutralize free NaOH. After its neutralization, the pH value decreases rapidly to reach values of 7 and subsequently 2. The pH changes as a function of the volume of sulfuric acid added and changes slowly during the neutralization of free NaOH. The pH is monitored throughout the reaction stage. Figure 3 shows the variation of pH with sulfuric acid volume.

## 8. Discussion of pH Effects

Regarding the effect of pH on the solubility of various substances in spent caustic, the composition initially has a pH of 14. The pH value decreases with sulfuric acid addition. Sulfide and thiosulfate compounds are predominant at pH values of 9–10. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) is

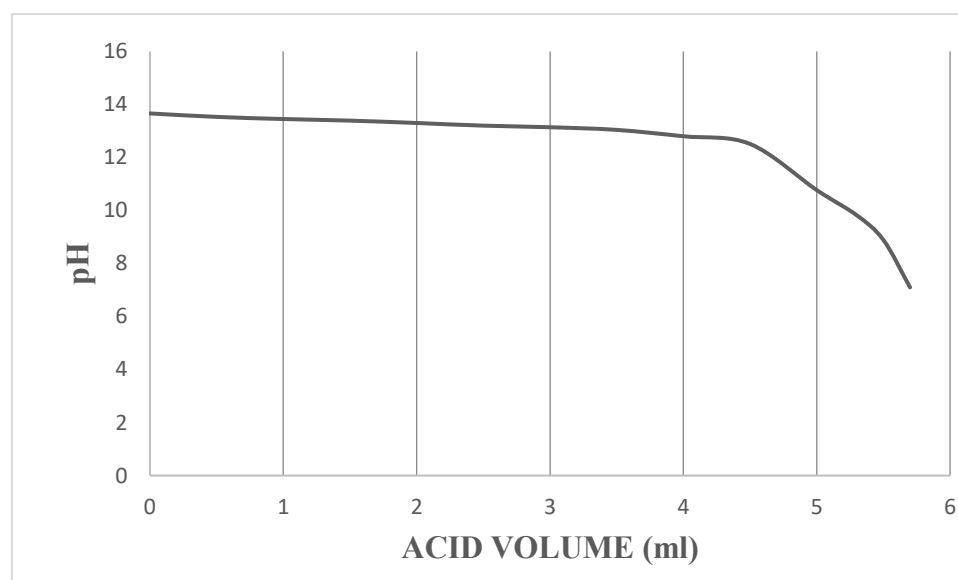
stable at pH 7. Therefore, the neutralization process requires reaching pH 7 and subsequent acidification to ensure complete neutralization.

The variation of pH with acid volume is shown in Figure 3. With increasing acid volume, the pH of spent caustic decreases to acidic values. COD reduction is also a function of mixing time, and lower mixing times (e.g., 0.5 min) result in greater COD reduction.

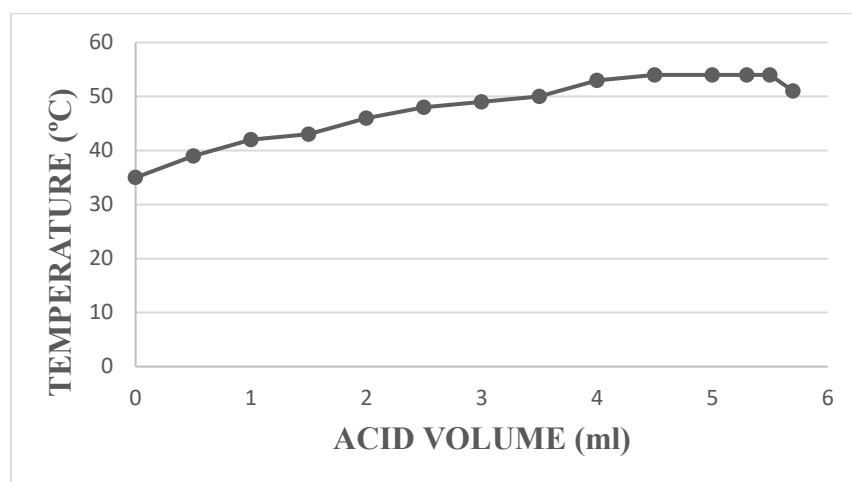
During neutralization of spent caustic with sulfuric acid, compounds such as sodium sulfide may produce corrosive and toxic  $H_2S$  gas. Proper management of this gas is required. Additionally, sulfuric acid can react with iron in tanks and equipment, leading to the release of dangerous hydrogen gas.

## 9. Recommendations for pH Management

During sulfuric acid neutralization, the pH value is continuously monitored. The pH decreases from 14 to 7 and finally reaches 2, while the COD value decreases from 34,000 to 8,000 ppm.



**Figure 3.** The change of pH of spent caustic solution with the amount of acid is plotted.

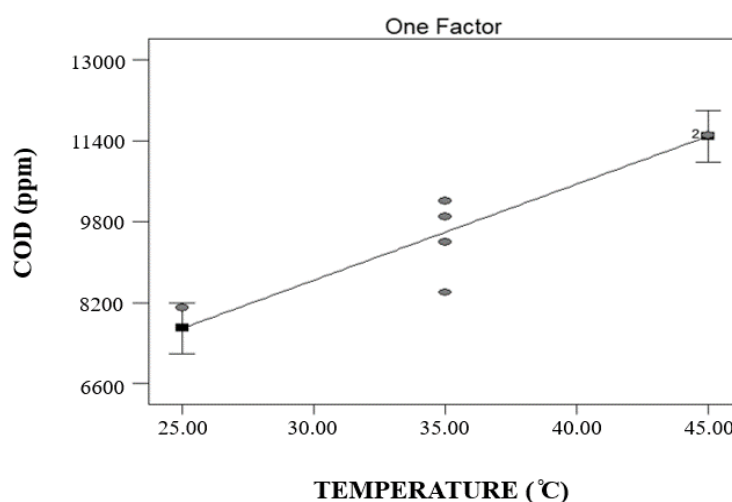


**Figure 4.** The change of temperature of the spent caustic solution with sulfuric acid value is plotted.

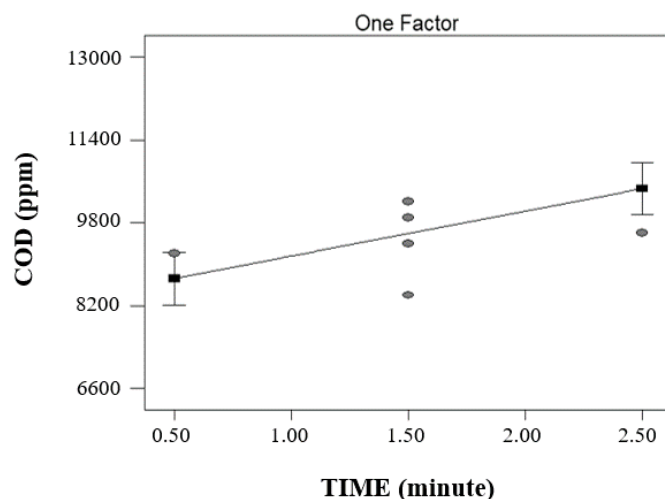
As depicted in Figure 3, by adding acid to a solution of sulfidic spent caustic, the pH initially does not change significantly; with increasing acid addition, the pH begins to change slightly.

In Figures 3 and 4, since the numbers are volume-based values and provide accurate information about the amount of sulfuric acid consumed, and are expressed in decimal form based on feed volume or acid concentration, the numbers have been retained in this form to clearly indicate sulfuric acid consumption. It is also worth noting that COD reduction is associated with decreasing pH and neutralizing sulfide, carbonate, and thiosulfate species and is not a function of acid volume.

In Figure 4, the temperature increases with increasing sulfuric acid addition to the sulfidic spent caustic solution due to heat release during the reaction (Figures 5 and 6).



**Figure 5.** The spent caustic COD changes relative to temperature at constant mixing time.



**Figure 6.** The spent caustic COD changes relative to mixing time at constant temperature.

Figure 5 and Figure 6 show COD changes in relation to temperature and mixing time, respectively. The gradient of the COD versus temperature curve at constant time is higher than that of the COD versus mixing time curve at constant temperature, indicating that temperature has a greater effect on COD reduction than mixing time due to solubility effects. The effect of mixing time also indicates that shorter mixing times are more effective than longer ones; in other words, lower reaction times are preferable for the neutralization process. Table 5 presents the analysis of outlet spent caustic after sulfuric acid injection, showing that sulfuric acid converts the components into sulfate salt forms.

**Table 5.** Anion and cation analysis of neutralized spent caustic with sulfuric acid.

Structure	Analysis
H <sub>2</sub> O	79%
Na <sub>2</sub> S, Sulfide, S <sup>2-</sup>	<1 ppm
Amount of sulfur in mercaptan (RSH-S)	<1 ppm
Cl <sup>-</sup>	540
SO <sub>3</sub> <sup>2-</sup>	<1 ppm
SO <sub>4</sub> <sup>2-</sup>	12%
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	460 ppm
PO <sub>4</sub> <sup>2-</sup>	<1 ppm
NO <sub>3</sub> <sup>-</sup>	236 ppm
NO <sub>2</sub> <sup>-</sup>	480 ppm
Thiocyanate	<1 ppm
NaOH	-

Analyzing Method	Ion Exchange Chromatography (IEC)
Equipment Brand	METROHM brand ion chromatography anion mode includes measurement of thiosulfate, thiocyanate,

## DISCUSSION

This study effectively treated spent caustic with sulfuric acid. Spent caustic received from phases 4 and 5 of Assaluyeh at the South Pars gas field of Iran was analyzed for anion and cation, then its COD and TDS values were measured. The COD value was 34,400 ppm, and the TDS value was 137,000 ppm. In the neutralization reaction of spent caustic with sulfuric acid, free caustic is first neutralized, then carbonates, sulfides, and thiosulfates are converted to sodium sulfate. Sodium sulfate salts precipitate as a salt after saturation. As a result of salt production and precipitation, the TDS value of the solution increases. The pH of the reaction also changes slowly from the initial value of spent caustic, which is 14, at first (the neutralization stage of free caustic), and then changes with a steep slope and reaches a neutral value of 7. This value occurs when sodium sulfate salt is formed. Adding more acid will make the environment acidic. By neutralizing the above materials, the pH value decreases from a high value of 12 to 7 and finally to 2. According to the explanations given, the COD value in different stages ranges from 34,400 ppm to about 20,000 ppm in the neutralization stage (pH 7) and to 8,000 ppm in the acidic stage (pH 2).

The sulfuric acid neutralization method is a simple method for treating spent caustic. The disadvantage of the method is the release of toxic gases such as H<sub>2</sub>S and corrosion problems. The sulfuric acid neutralization method is a convenient method compared to other methods of treating spent caustic and can be easily commercialized. After the sulfuric acid reacts with spent caustic, all the components in it are converted to sulfate.

## FUTURE WORK SUGGESTIONS

In this paper, only the effect of mixing time between sulfuric acid and spent caustic was investigated. It is necessary to investigate the effect of pH, total reaction time, temperature, and mixing rate (stirring speed) in future research.

## CONCLUSION

Spent caustic is a hazardous chemical waste that is produced in oil, gas, and petrochemical industries. Fuel treatment with caustic and separation of mercaptans and hydrogen sulfide causes the transfer of sulfur compounds to fresh caustic, which is accomplished. Spent caustic is regenerated in a closed-cycle loop back to caustic. Continuing this absorption/regeneration loop increases the salts in the caustic. Drainage of this caustic produces spent caustic. Treatment of spent caustic with sulfuric acid is one of the simplest methods that is used in industry. Adding acid will convert sulfidic compounds to sulfate salts and precipitate them in the solution. The major problems of the neutralization process for spent caustic are the production of toxic hydrogen sulfide and corrosion in equipment. pH changes during the neutralization process start from a maximum value of 14 and are reduced to 12 by neutralizing the free caustic. After neutralizing the free caustic, other materials in the spent caustic composition, including carbonates, sulfides, and thiosulfates, enter into the reaction.

By neutralizing the above materials, the pH value decreases from a high value of 12 to 7 and finally to 2. According to the explanations given, the COD amount in different stages ranges from 34,400 ppm to about 20,000 ppm in the neutralization stage (pH 7) and to 8,000 ppm in the acidic stage (pH 2).

The draining of treated spent caustic to the environment is not allowed, as the COD and TDS are still high. The optimization of the neutralization process has been investigated in this paper. The results show that the temperature of acid and spent caustic mixing time and reaction time are variables that affect the process, and temperature is more effective than mixing time for COD reduction. For optimization of the process and design of experiments, the central composite design method was used, and a linear model for COD reduction with mixing time and temperature is proposed by the CCD method. Due to the simplicity of the spent caustic neutralization method with sulfuric acid, the above method has been developed in the industry.

## NOMENCLATURE

[COD] Chemical Oxygen Demand (ppm or mg/l)

[BOD] Biochemical Oxygen Demand(ppm or mg/l)

[TOC] Total organic carbon(ppm or mg/l)

[TOD] Total oxygen demand(ppm or mg/l)

[TDS] Total Dissolved Solids (ppm or mg/l)

[TOC] Total Organic Carbon (ppm or mg/l)

[LPG] Liquefied Petroleum Gas

[RTECS] Registry of Toxic Effects of Chemical Substances

[WGK] Water Hazard Class

[ML] milli liter

[BOD] Biological Oxygen Demand (ppm)

[CCD] Central Composite Design method

[A] mL FAS used for free sample

[B] mL FAS used for the sample

[M] molarity of FAS

[8000] mill equivalent weight of oxygen  $\times 1000$  mL/L

[FAS ] Ferron Indicator

## References

[1] Li. Jianwei, Li Xiang., Liu Yan, Zhang Jie,). Removal of mercaptans from light oils using ionic liquid–NaOH aqueous solution as extractants. Chinese journal of chemical engineering. 25, no. 2: 171-174, 2017.

[2] C Maugans,, M.Howdeshell, , S De Haan,. Update: Spent caustic treatment. Hydrocarbon processing 89, no. 4: 34-38. 2010.

[3] Hawari, Alaa, Hasanat Ramadan, Ibrahim Abu-Reesh, Mabrouk Ouederni. A comparative study of the treatment of ethylene plant spent caustic by neutralization and classical and advanced oxidation. Journal of environmental management. 151: 105-112 ,2015.

[4] A.Karimi, , E., Fatehifar R Alizadeh,, , I. Ahadzadeh Regeneration and treatment of sulfidic spent caustic using analytic hierarchy process. Environmental Health Engineering and Management Journal. 3, no. 4: 203-208. 2016.

[5] Spent Caustic treatment with OHP Wet Peroxide Oxidation, FMC Foret,Plaza Xavier cugat, 2 edificio c,plant 308174 sant cugat del valles(Barcelona)Espana Email:ohp@fmc.com, [www.fmcforet.com](http://www.fmcforet.com).

[6] Marco De Graaff, , Klok Johannes BM, Martijn FM Bijmans, Gerard Muyzer, Albert JH Janssen. Application of a 2-step process for the biological treatment of sulfidic spent caustics. Water research. 46, no. 3: 723-730. 2012.

[7] A.Farzi, , Bayram, S.Moslemi ,Treatment of ethylene spent caustic pollutant using sulfuric acid. International journal of scientific and engineering research. 6. 2015.



- [8] A.Gameel, , G Malash,, A Mubarak,. M.Hussein, Treatment of spent caustic from ethylene plant using electro-Fenton technique. American Journal of Environmental Engineering and Science. 2, no. 4: 37,2015.
- [9] Carlos Tania, S Mara., Refinaria de Petroleos de ManguinhosWet air oxidation of refinery spent caustic: a refinery case study. In NPRA Conference. . 2000.
- [10] A. M Pisarevsky,, I. P Polozova,, P. M Hockridge,. Chemical oxygen demand, Russian Journal of applied chemistry, 78, 101-107. 2005.
- [11] American society for testing and materials, Standard test methods for chemical oxygen demand (dichromate oxygen demand) of water. D1252-95, ASTM Annual Book of Standards. American Soc. Testing & Materials, Philadelphia, Pa. 1995.
- [12] Z,Mohammadizadeh A Farshi., S.J,Roayae N. Jodeiri, Investigation treatment of Gas-Condensate Spent caustic of south pars phase 4&5 refinery by Catalytic Oxidation Method and optimization of parameters , MS Dissertation , Sahand University of Technology,2018.
- [13] Z Mohammadizadeh, A.Farshi S.J, Roayae, N., Jodeiri,,An extensive review on spent caustic treatment methods in oil and gas industry , Iranian Chemical engineering journal (Persian language),Vol.17, NO. 96, 2018.