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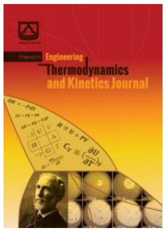
Progress in Engineering Thermodynamics and Kinetics Journal

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



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

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ARTICLE INFO

Keywords:

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

ABSTRACT

Spent caustic is one of the most harmful wastes of refineries, gas and petrochemical industrial processes. Considering the CCD optimization methods, various experiments were conducted to neutralize the spent caustic and then using the design expert software, the process parameters including initial temperature and reaction time were considered as effective parameters. The COD neutralization process was modeled as a linear equation. 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. All sources of harmful components of the spent caustic were converted to sulfate salts. The industrial limit for spent caustic wastewater is that the COD value should be in the range of 60-100 ppm. However, this value is difficult to achieve and is usually achieved by diluting the final spent caustic wastewater. pH changes during the neutralization process started from a maximum value of 14 and was reduced to 12 by neutralizing the free caustic values.. According to the explanations given, the COD amount in different stages ranges from 34,400 ppm to about 20,000 in the neutralization stage (pH 7) and to 8,000 in the acidic stage (pH 2).By neutralizing the above materials, the pH value decreases from a high value of 12 to 7 and finally to 2.

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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*. https://doi.org/10.22075/JPETK.2025.

INTRODUCTION

Spent caustic has an unpleasant odor due to the presence of sulfide salts, mercaptans, and organic materials such as disulfides, and has severe corrosive effects due to the presence of such materials. The possibility of discharge into the environment due to the presence of toxic substances and high COD is not allowed by environments organization. Therefore, spent caustic treatment and removal of toxic substances with COD reduction should be done. Types of spent caustics according on the different petroleum cuts and treatment process are classified into three type of (1) sulfidic spent caustic (2) cresylic spent caustic (3) naphthenic spent caustic. There are several methods for treating of spent caustic, which in this paper, neutralization with sulfuric acid is investigated. Due to the presence of organic loads, minerals and suspended solids and different salts in spent caustic, COD of spent caustic is high in these compounds and for COD reduction of this type of spent caustic to acceptable environmental values a combined treatment processes are required. Sulfidic spent caustic of south pars gas refinery have COD equal to the values of 34400 ppm.

The presence of mercaptans in light/heavy petroleum product and natural gas causes fresh caustic to be inactivated (converted to spent caustic) during demercaptanization process of petroleum product, since the caustic solution is used to removed mercaptan and other undesirable compounds from petroleum refining product [1, 2]. After removing the mercaptans from hydrocarbons stream, caustic solution converted to the spent caustic [2, 3]. Then spent caustic is sent to regeneration process until spent caustic is regenerated. As spent caustic circulates in the absorption/regeneration loop, eventually salts and impurities increase the amount of spent caustic, and to refresh the caustic concentration in the spent caustic liquid circulation loop, it must be drained. This drained liquid is called spent caustic**.** [4]

. In addition to the refinery industry, other industries, including LPG, natural gas (methane) treatment units also produce spent caustic. The most dangerous substance present with spent caustic when neutralized with sulfuric acid is hydrogen sulfide, which is highly toxic and deadly and has a foul odor. Due to harmful impurities, it is not possible to disposal spent caustic to the environment for disposal it COD value should be reach 60 ppm. [2]. Spent caustic are generally categorized into three types: sulfidic, cresylic and naphthenic [2, 3]. Sulfidic spent caustic contains sulfur (0.5-4%), mercaptans (0.1-4%) and naphthenic spent caustic contains naphthenic acid (15% in diesel), low amount of sulfide and cresylic spent caustic that is rich in phenol, cresols and organic acids [5]. Spent caustic due to alkalinity, salinity, high levels of sulfide and toxic sulfur compounds such as methyl mercaptan (methantiol) and aromatic hydrocarbons such as benzene is hazardous to the environment and should be treated [6]. Methods of spent caustic treatment are categorized as following: Deep well injections, Incineration, Wet air oxidation, advanced oxidation, biological treatment, catalytic oxidation, coagulation, neutralization [2, 7]. Hawari a. et al. [3], investigated ethylene plant spent caustic of Qatar Petrochemical Company. They compared three methods of 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%) were achieved. In the classical oxidation method the maximum removal rate of COD at pH = 2.5 and the concentration of 19 mM / L hydrogen peroxide is reached to 89%. With higher hydrogen peroxide concentration, COD removal is reduced, so the concentration level of hydrogen peroxide to be increase. In the advanced oxidation the highest COD removal at pH =2.5 and the ratio of hydrogen peroxide to iron sulfate (7: 1) is reached to 96.4%. The highest percentage of COD removal (96%) was achieved by advanced oxidation. De Graaff M. et al. [6], during study on biological treatment of spent caustic found that the 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 A. et al. [7], after neutralizing Tabriz petrochemical spent caustic with sulfuric acid, they concluded that the proposed method was low costs and have a good reaction rate at the medium temperature and atmospheric pressure. It produces valuable products such as sodium sulfate, and optimum temperature and time is 45 ° C and 2 minutes, respectively. In this experiment, the color and phenol content are reduced in 30 minutes and the initial temperature has a great effect on the treatment process. Gameel A. et al. [8], performed the electro-Fenton treatment method using iron and stainless steel electrodes for spent caustic treatment of the Sidi Karir petrochemical company in Alexandria, Egypt, and achieved the following results: Flow density, H2O2 concentration, reaction time, initial pH and state of the adding H2O2 are effective parameters on efficiency in this method. Flow density and H2O2 concentration have a direct correlation with COD removal efficiency, but excessive increase leads to a reduction in COD removal. Primary pH is also an important factor in this process, which pH=3 is the optimal pH in this process. Also, if H2O2 is added continuously, it has a positive effect on COD removal. Carlos t. et al. [9], used a wet air oxidation method to treat the refinery spent caustic, which is the best method because that removed the unpleasant odor. After wet air oxidation, the reactor effluent is discharged into biological treatment section. But shall be emphases that wet air oxidation process due to high investment cost and dangerous operating condition have limited application.

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. All sources of harmful components of the spent caustic were converted to sulfate salts. The industrial limit for spent caustic wastewater is that the COD value should be in the range of 60-100 ppm. However, this Spent caustic reaction with sulfuric acid is fast, it suddenly reacted and large amount of gas are produced, so neutralization process should be carried out very slowly and with caution. When the sulfuric acid reacts with spent caustic, it precipitates salt, which is sodium sulfate. In neutralizing of spent caustic with sulfuric acid, in addition to removing waste, it also produces a valuable substance, such as sodium sulfate [7]. The reactions of spent caustic with sulfuric acid are as follows: By adding sulfuric acid to caustic solution, sodium bisulfate and then sodium sulfate are formed:

$$H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O \tag{1}$$

$$NaHSO_4 + NaOH \rightarrow Na_2SO_4 + H_2O \tag{2}$$

As in spent caustic solution quantities (moles) of sodium hydroxide are greater than moles of acid, by adding sulfuric acid to the caustic solution, sodium sulfate is first formed, by adding more acids to the solution, sodium bisulfate according reaction no.4 same as reaction no.1 as acid salt will be produced.

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + H_2O \tag{3}$$

$$H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O \tag{4}$$

Therefore, the reaction numbers 3 and 4 are suitable for treatment of waste water because for the production of sodium sulfate salt, with one mole of acid the two moles of caustic solution were required. According above clarification it can be concluded that sodium sulfate is the reaction salt and if solution is saturated with them it will be precipitated in solution. Also, sulfuric acid can have reaction with existing sodium carbonate, sodium thiosulfate and sodium sulfite to convert them to sodium sulfate according to below reactions:

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2 \quad (5)$$

$$Na_2S_2O_3 + H_2SO_4 \rightarrow Na_2SO_4 + S(s) + SO_2(g) + H_2O \quad (6)$$

$$Na_2S + H_2SO_4 \rightarrow Na_2SO_4 + H_2S \quad (7)$$

According to reaction number 7, sodium sulfide will converted to sulfate of sodium and H_2S. Producing H_2S is not good from health and corrosion view point as H_2S is toxic will be effect on personals health and also it will have corrosion effect on reactors and accessories. According above reactions(no.3&7) for 100 mL of spent caustic the following value of sulfuric acid (density 1.84gr/ml) is required:

1- 5.03 mL equal to 0.09444grmole of sulfuric acid for the reaction no.3
2- 0.31 mL equal to0.005820grmole of sulfuric acid for the reaction no.7.

EXPERIMENTAL SET-UP AND METHOD [12]

The experimental schematic diagram of the present study is depicted in figure 1**.**

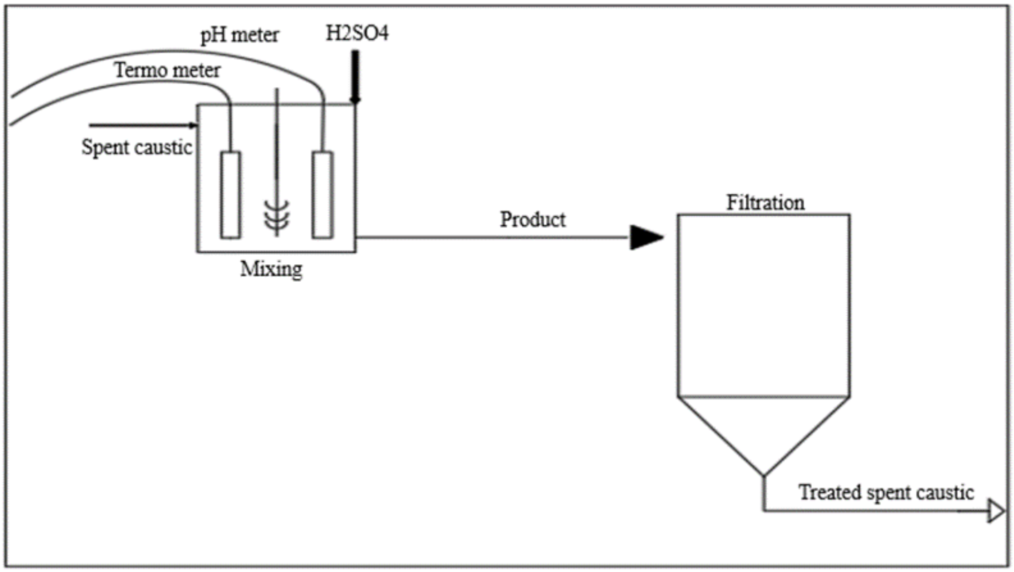

Figure 1. Experimental schematic diagram including flowing step, first step (left side of figure) (1) A glass mixing vessel with agitator and heater, second step right side of figure (2) filtrated system with vacuum pump

First, 100 mL of the spent caustic was added in glass vessel, equivalent to 107.72 gr, and connected the stirrer to mixed at 320 rpm and insert the pH meter into the beaker so that the pH of solution can be detected, the pH value is changes at any time. The acid was added slowly after adding acid temperature will rise it is waited between 0.5 and 2.5 minutes depending on the test conditions to make the reaction temperature stable. The feed is also tested at three different temperatures (25, 35 and 45°C) and atmospheric pressure. The titration process was continued until the pH value reached to 7. The temperature of solution was measured by thermometer. After finishing reaction the reminded solution are filtrated with use of filter paper and vacuum pump. The reminded solution is treated product. A sample of solution is send to laboratory for measurement of Chemical Oxygen Demand (COD). The Chemical Oxygen Demand (COD) method determines the quantity of oxygen required to oxidize the organic matter in a waste sample, under specific conditions of oxidizing agent, temperature, and time. Chemically combined oxidants (such as reducing chemicals) that enter natural water, similarly show chemical reactions. This type of chemical reaction creates a chemical need for oxygen called COD. As a result, the COD of a sewage, wastewater or contaminated water is the amount of oxygen needed to oxidize the oxidation material contained therein. The amount of COD is usually measured using a potent oxidizing agent in the acidic environment. Pollutant that can’t be oxidized by oxygen, it can be oxidized by microorganism, that it called biological oxygen demands (BOD) [10].

MATERIALS AND METHODS

Spent caustic and sulfuric acid are chemical materials that were used in this research. Spent caustic produced in phases 4 and 5 of Assaluyeh at south pars gas field of Iran. The specification of anion and cation components and other chemical properties of spent caustic are given at Table 1.

Table 1: Spent caustic chemical properties of south pars gas refinery of phase 4&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, reflux and titrate a blank containing the reagents and a volume of distilled water equal to that of sample. Exercise extreme care with this procedure because even a trace of organic matter on the glassware or from the atmosphere may cause gross errors. If a further increase in sensitivity is required, concentrate a larger volume of sample before digesting under reflux as follows: Add all reagents to a sample larger than 50 mL and reduce total volume to 150 mL by boiling in the refluxing flask open to the atmosphere without the condenser attached. Compute amount of H_2SO_4 to be added (before concentration) on the basis of a weight ratio of 10:1, H_2SO_4: Cl^- using the amount of Cl^- present in the original volume of sample. Carry a blank reagent through the same procedure. This technique has the advantage of concentrating the sample without significant losses of easily digested volatile materials. Hard-to-digest volatile materials such as volatile acids are lost, but an improvement is gained over ordinary evaporative concentration methods. Determination of standard solution: Evaluate the technique and quality of reagents by conducting the test on a standard potassium hydrogen phthalate solution [11].

$$\text{COD as mg } O_2/L = \frac{(A-B)*M*8000}{\text{mL sample}} \tag{8}$$

EXPERIMENTAL DESIGN METHOD

For optimization of number of test in laboratory research project experimental design methods are used. There are different experimental design and evaluation methods. One of methods is Central Composite Design (CCD) method. In statistics, a central composite design is an experimental design, useful in response surface methodology, for building a second order (quadratic) model for the response variable without needing to use a complete three-level factorial experiment. After the designed experiment is performed, linear regression is used, sometimes iteratively, to obtain results. Coded variables are often used when constructing this design. A Box-Wilson Central Composite Design, commonly called 'a central composite design', contains an imbedded factorial or fractional factorial design with center points that is augmented with a group of 'star points' that allow estimation of curvature. If the distance from the center of the design space to a factorial point is ±1 unit for each factor, the distance from the center of the design space to a star point is $|\alpha| > 1$. The precise value of α depends on certain properties desired for the design and on the number of factors involved. Similarly, the number of center point runs the design is to contain also depends on certain properties required for the design. In this study central composite design (CCD) method was used for design of experiments. Two factors were used as input variables like time of reaction and initial temperature. The ranges of input variables are depicted 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).

RESULTS AND DISCUSSION

The design laboratory data table according to CCD method and result of experimental data for COD is depicted at Table 3. In Table 3 the highlight parts of the experiments are repeated. The design of experimental for this process is done by the Quadratic model [12].

Table 3. Design of laboratory data table according to CCD method and 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 of this design of experimental is reported at Table 4.

Table 4. Analysis of variance of 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 is suitable for this design. P value of both factors is less than 0.05, so both factors have a greater impact on the process. The term of inappropriateness is also not appropriate, therefore the factors are in proportion to each other. Figure 2 shows the prediction and actual chart of this process. At Figure 2 the depicted value of COD according to model and experimental data were compared with each other.

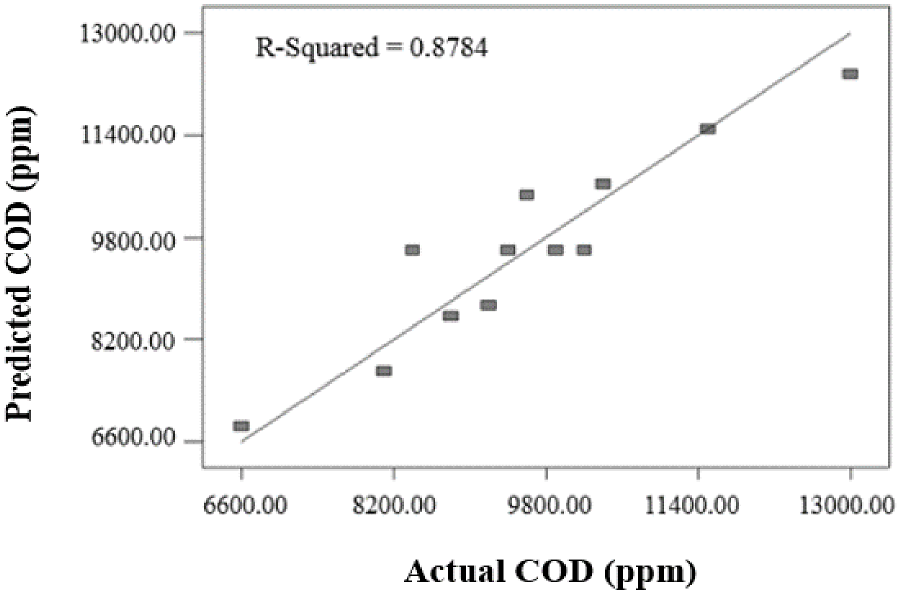

Figure 2. Predicted vs. Actual value of spent caustic COD is shown

As depicted in figure 2 the R-Squared value is close to 1 and is approximately appropriate. The final equation obtained for measuring the COD of the spent caustic using the factors is given at Equation 9.

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

With the optimization results of the design experimental, it is observed that by decreasing the initial temperature and mixing time, the COD value also decreases because at higher temperatures, the solubility of pollutants in the spent caustic is higher and COD does not decrease (Figure 3 ,4 and 2), but when the initial temperature is lower, the solubility of salts will be also lower and the COD decreases further. The optimum point is at temperature 25 ° C and mixing time 0.5 min, with a COD value of 6600 ppm. The values of the acid-pH value and the acid-temperature value against to sulfuric acid amount are depicted in Figure 3 and Figure 4, respectively, for the average interval test.

Impact of pH on Reaction Efficiency

The pH of Spent caustic soda is about 14. The pH is reduced by adding sulfuric acid to it. Initially, the amount of acid is used to neutralize the free caustic soda, and in this case the pH value does not change much. When the free caustic soda is neutralized, the pH changes a lot, in this case the other components are neutralized and the pH value changes accordingly. The substances in spent caustic include carbonates, sulfides, and sulfates with different compounds. In the neutralization stage, after the pH of 14, with adding acid pH value reaches 12 and then quickly reaches a neutral value of 7 when free NaOH is neutralized totally. By adding acid, its value reaches about 2. The greatest COD reduction is at pH equal to 2.

Monitoring pH Changes

The amount of spent caustic starts to change from the initial value of 14. Usually the pH value changes due to the addition of sulfuric acid. A large initial amount of sulfuric acid is used to neutralize the NaOH caustic. After its neutralization, the pH value changes rapidly to reach values of 7 and 2 respectively. pH is change according adding amount of volume of sulfuric acid and it is slowly go on during stage of neutralization NaOH on free phase. pH is monitored on reaction stage. Figure 3 shows pH change with volume of sulfuric acid.

Discussion of pH Effects

Regarding the effect of pH on the solubility of various substances in spent caustic, the composition itself has a pH of 14 in its initial state. The pH value is reduced by adding sulfuric acid. Also, sulfide and thiosulfate compounds are at pH 9 to 10. Sodium sulfate salt Na2so4 is also stable at pH 7. Therefore, in the neutralization process, pH 7 must be reached and the mixture must be acidified to ensure complete neutralization at figure 3 of manuscript variation of pH with acid volume is shown. With increasing acid volume pH of spent caustic at last will decrease to reach acid pH. The level of COD reduction is function of mixing time. With low mixing time as 0.5min COD level reduction will be high.

In the neutralization operation of SPENT CAUSTIC with sulfuric acid, the presence of compounds such as sodium sulfide in spent caustic and its neutralization with sulfuric acid can lead to the production of corrosive and toxic gas H2S. In this case, it is necessary to manage the above toxic gas properly. The reaction of sulfuric acid with the iron of tanks and equipment can lead to the release of dangerous hydrogen gas.

Recommendations for pH Management

During the process of neutralizing spent caustic with sulfuric acid, the pH value changes. The pH value is measured by a pH monitor. The pH value of spent caustic drops from 14 to 7 and finally reaches 2. The COD value of spent caustic drops from 34,000 to 8,000 ppm.

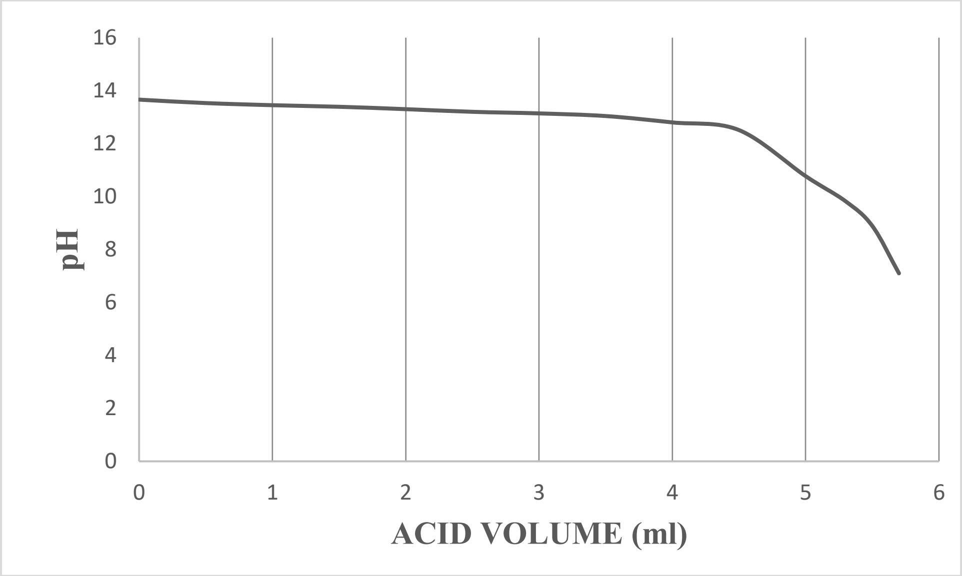

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Figure 3. change of pH of spent caustic solution with acid amount is plotted

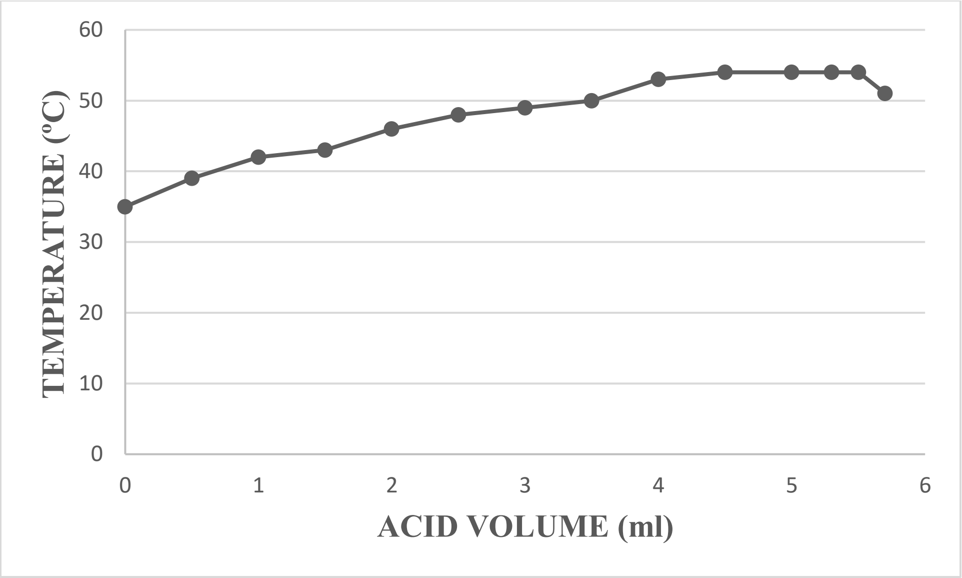

Figure 4. Change of temperature of spent caustic solution with sulfuric acid value is plotted

As depicted in Figure 3, by adding acid to a solution of sulfidic spent caustic at first, pH does not change significantly, with the increase in the amount of acid, the pH begins to change slightly.

In Figures 3 and 4, since the numbers are volume numbers and give accurate information about the amount of sulfuric acid consumed and are converted to decimals by dividing the feed volume or acid concentration, the numbers have been retained in the above form to clearly indicate the amount of sulfuric acid. It is also worth noting that the basis for COD reduction is based on reducing the pH value, neutralizing sulfide, carbonate, and thiosulfate substances, and etc. is not a function of the volume of acid.

In Figure 4, the temperature also increases by increasing the amount of acid added to the sulfidic spent caustic solution, which is due to heat release during the reaction. (figures 5,6).

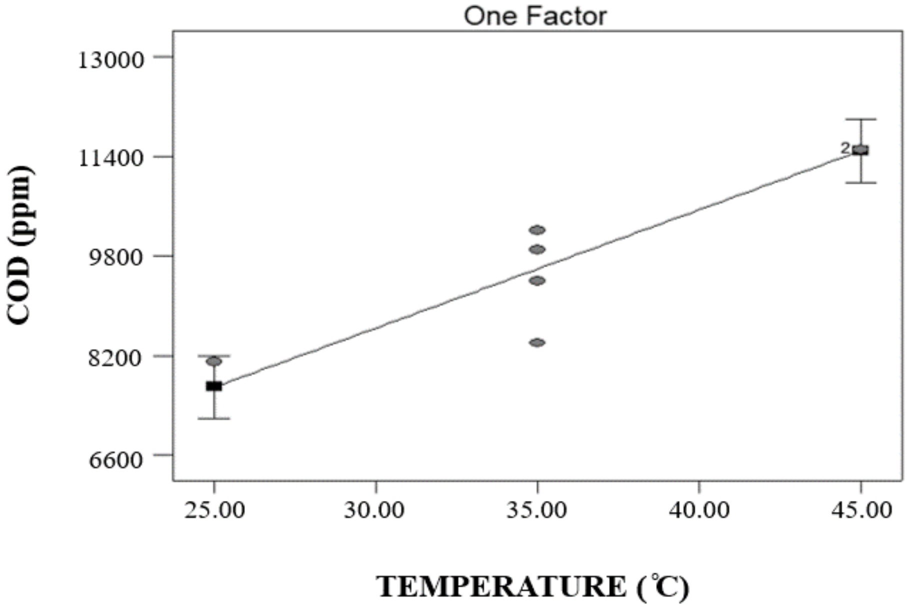

Figure 5. spent caustic COD changes relative to temperature at constant mixing time

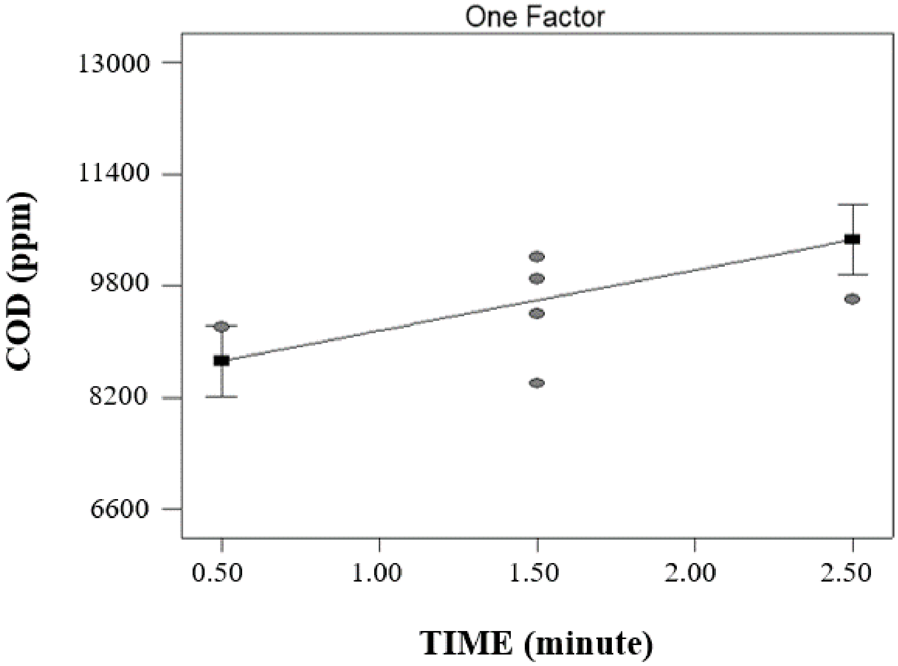

Figure 6. spent caustic COD changes relative to mixing time at constant temperature

Figure 5 and Figure 6 show COD changes in relation to temperature and time of mixing (at constant temperature), respectively. As can be seen, the gradient of the COD and the temperature chart at constant time is higher than the COD and time chart at constant temperature, this means that the effect of temperature on the COD change is greater than the mixing time it is due to the solubility factor. Also from effect of mixing time on COD change it is depicted that small mixing time is better that large mixing time on the other means low reaction time is better that high reaction time for neutralization process. Also, at Table 5 analysis of outlet spent caustic after injection of sulfuric acid process is depicted. As analysis of data depicted sulfuric acid will convert and change all molecule to sulfate salt states.

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

Structure	**Analysis**
H_2O	79%
Na_2S, Sulfide, S^{2-}	<1 ppm
Amount of sulfur in mercaptan (RSH-S)	<1 ppm
Cl^-	540
SO_3^{2-}	<1 ppm
SO_4^{2-}	12%
$S_2O_3^{2-}$	460 ppm
PO_4^{2-}	<1 ppm
NO_3^-	236 ppm
NO_2^-	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 treats SPENTCAUSTIC with sulfuric acid, spent caustic received from phase 4&5 was analyzed for anion and cation, then its COD and TDS values were measured, COD value is 34400ppm, TDS value is 137000ppm.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 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, and this value is when sodium sulfate salt is formed. Adding acid to another amount 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 amount in different stages ranges from 34,400 ppm to about 20,000 in the neutralization stage (pH 7) and to 8,000 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 H2S 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. The acid converts all the components in it to another form.

FUTURE WORK SUGGESTIONS:

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

CONCLUSION

Spent caustic is a hazard chemical waste that will produced in oil/gas/petrochemical industrial. Fuel treatment with caustic and separation of mercaptans and hydrogen sulfide causes transferring of sulfur compound to fresh caustic were accomplished. spent caustic was regenerated in close cycle loop to caustic with continuing this absorption/regeneration loop amount of salts were increased in caustic, drainage of this caustic produced spent caustic. Treatment of spent caustic with sulfuric acid is one of simple methods that was used in industrial. Adding acid will be converted sulfidic compound to sulfate salts and precipitated in solution. The major problems of neutralization process of spent caustic are producing hydrogen sulfur toxic gas and corrosion in equipment. pH changes during the neutralization process started from a maximum value of 14 and was reduced to 12 by neutralizing the free caustic values. After neutralizing the free caustic values, other materials in the spent caustic composition, including carbonates, sulfides, and sulfides, 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 in the neutralization stage (pH 7) and to 8,000 in the acidic stage (pH 2).

The draining of treated spent caustic to environments is not allowed as the COD and TDS are still high. The optimization of naturalization process has been investigated in this paper, the result showed that temperature of acid &spent caustic mixing reaction time are variables parameters and temperature is more efficient than mixing time on COD reduction. For optimization of process and design experiments central composite design method is used and a linear model for COD reduction with mixing time and temperature is proposed by CCD methods. 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 sample

[M] molarity of FAS

[8000] mill equivalent weight of oxygen × 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.
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,Roayaee 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 Technolo y,2018
13. Z Mohammadizadeh, A.Farshi S.J, Roayaee, 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