

Treatment of ethylene spent caustic pollutant using sulfuric acid

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Abstract— Caustic soda is used in naphtha cracking units and petroleum refineries for sweetening of hydrocarbon streams. The generated caustic waste is an environmental pollutant and must be removed. Several methods are proposed for treatment of spent caustic such as wet air oxidation, biological treatment, etc. Spent caustic used in this work is prepared from Tabriz Petrochemical Company. In this work sulfuric acid was used for treatment of spent caustic which not only removes the waste, but also generates valuable product of sodium sulfate. In each experiment, 1L of spent caustic was taken and its color and phenol were removed by oxidation with H₂O₂. Then, 50 mL sulfuric acid was added and treatment process was performed. Different samples were taken at specified time periods to calculate percent waste conversion. The results showed that after 2.5 minutes it was about 79%, 84% and 92% at 25, 35 and 45°C, respectively.

Index Terms— Spent caustic treatment, Sulfuric acid, Sodium sulfate, Response surface methodology, Analysis of variance

1 INTRODUCTION

CAUSTIC soda is used in petroleum refining and chemical industries to remove sulfur compounds from hydrocarbon streams. The resulting solution is usually referred to as spent caustic and is deposited into the environment. Spent caustic is usually composed of sodium hydroxide, water, sulfur compounds and other pollutants [1].

There are two types of spent caustic in the industries:

a) *Ethylene spent caustic*. Naphtha feed entering naphtha cracking unit consists of hydrogen sulfide and carbon dioxide which are removed in a scrubbing column by using caustic soda and as a result, sodium hydrosulfide, sodium carbonate and other pollutants such as mercaptanes, sulfides, carbonates and small amounts of organic compounds are produced [2].

b) *Refinery spent caustic*. It is produced from different sources such as Merox process on diesel, Merox process on kerosene or jet fuel, and also Merox process on LPG [3]. In these processes, sulfides and organic acids are chemically absorbed by caustic soda. Caustic soda is consumed and generated cresylic and naphthenic acids, and mercaptides are mixed and spent caustic is produced [3].

Several methods have been proposed for treatment and removal of spent caustic. Masoomian [2] presented a method for treating and regenerating ethylene spent caustic. The method includes oxidizing spent caustic with an air/ozone gas mixture at ambient temperature and then irradiation of the product with a broad range of ultraviolet radiation and finally filtering spent caustic solution. The process can have great operating costs because of using ozone and ultraviolet radiation.

Ellis [4] used wet air oxidation (WAO) method for treatment of refinery spent caustic. It has the advantage of not producing odorous offgas. In a case study, COD of the effluent was decreased about 80% with pH of near 7 using this method without using acids for neutralization. The main disadvantage of this method is its high temperature and pressure operating conditions. Also De Angelo and Wilhelmi [1] and Chowdhury [5] used WAO method for spent caustic treatment.

Janssen, et al. [6] treated spent caustic biologically using aerobic bacteria together with redox potential in a gas-lift bioreactor. The capacity of biological processes is usually much lower than physical and chemical processes and because spent caustic is generated in large amounts a biological method must be combined with chemical or physical methods. Also Sipma, et al. [7] used a biological method for spent caustic treatment containing thiols. Thiobacillus aerobic isolate removes sulfuric components from spent caustic by oxidation reactions during biological metabolisms. H₂SO₄ produced by this microorganism will decrease pH of spent caustic solution [8].

Keramati, et al. [9] used electrodeionization method by the aid of ion exchange membranes. The main disadvantage of electro dialysis method is that it is only practical for solutions of low concentration. This problem can be overcome by combination of electro dialysis with ion exchange method. This improved method is called Electrodeionization [9]. Also, Wei, et al. [10], suggested Bipolar Membrane Electrodeionization (BMED) as a high efficiency spent caustic treatment method.

Other methods that have been investigated by authors include advanced oxidation using hydrogen peroxide or ozone [2, 11, 12], ozone and hydrogen peroxide with UV-vis [11], fenton [13, 14], and ion exchange resins [12].

2 MATERIAL AND METHODS

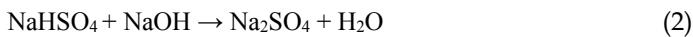
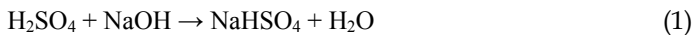
Spent caustic produced in olefin unit of Tabriz Petrochemical Company (IPC) has generated many problems such as refinement and operation costs and also environmental pollution. In this unit caustic soda is used for absorption of acid gases, namely CO₂ and H₂S, from naphtha feed and after oxidation and naturalization by HCl it is deposited into

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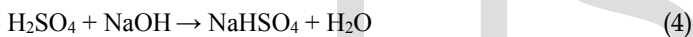
environment. Because of large amounts of waste disposal which is about 1000 L/hr, its regeneration or removal is necessary.

After vast investigation about different methods for spent caustic treatment, it was found out that the use of sulfuric acid could be a proper method for treatment of spent caustic. Because not only it removes spent caustic pollutants but also as it will be seen, the valuable product of sodium sulfate is produced during treatment process which can be sold. The usual method for preparation of sodium sulfate is its extraction from Mirabilite deposits found in the lakes or salty waters of the surface of a lake during fall and winter. Another method is injection of hot water into salty layers and dissolution and evaporation of Mirabilite and drying it in rotating driers [15].

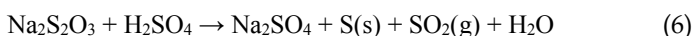
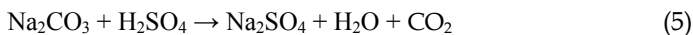
By adding caustic soda to sulfuric acid, firstly sodium bisulfate and then sodium sulfate salt is produced [16, 17]:



In opposite direction, i.e. by adding acid to caustic solution firstly sodium sulfate is generated because moles of sodium hydroxide are more than moles of acid. Adding more acid to the solution results in the generation of acidic salt of sodium bisulfate [16, 17].



Generally, second method must be used for spent caustic treatment because of the large amounts of the waste. According to Eq. (3), the required moles of sodium hydroxide is 2 times the moles of acid for generation of sodium sulfate. Also sulfuric acid can convert sodium carbonate and sodium thiosulfate to sodium sulfate based on the following reactions [17, 18].



As a result of the reaction between sulfuric acid and spent caustic, sulfur can be generated according to Eq. 6, which is because of the existence of sodium thiosulfate. It can be removed by oxidation with hydrogen peroxide [19].

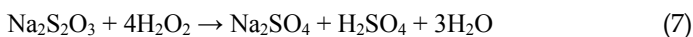


Table 2 shows concentration of different pollutants present in a 1 L sample of crude spent caustic obtained from TPC. Also Table 1 shows chemical components that were used in the experiments.

For preparation of the working solution, 1 L of spent caustic was taken and 20 mL of hydrogen peroxide was used for 30 min in order to remove its color and phenol content [20]. Then prepared spent caustic was analyzed using Palintest® photometer 7100 in order to detect composition of different

components within it. Fig. 1 shows spent caustic (a) before and (b) after oxidation by hydrogen peroxide.

TABLE 1
CHEMICAL COMPONENTS USED FOR PERFORMING EXPERIMENTS

Chemical component	Chemical formula	Application	Producer
Ammonium molybdate	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	Measurement of sodium thiosulfate	MERCK
Hydrochloric acid	HCl	Measurement of caustic	MERCK
Potassium hydrogen phthalate	$\text{C}_8\text{H}_5\text{KO}_4$	Measurement of sodium thiosulfate	MERCK
Phenolphthalein	-	Measurement of sodium carbonate	MERCK
Methyl orange	-	Measurement of sodium carbonate	MERCK
Hydrogen peroxide	H_2O_2	Phenol and color removal	MERCK
Sulfuric acid (98%)	H_2SO_4	Spent caustic treatment	MERCK

TABLE 2
CONCENTRATION OF DIFFERENT POLLUTANTS WITHIN 1 L OF SPENT CAUSTIC SAMPLE

Component	Concentration (ppm)
Na_2SO_4	6.3
Na_2CO_3	21.2
NaOH	5.1
$\text{Na}_2\text{S}_2\text{O}_3$	2.6
Phenol	3

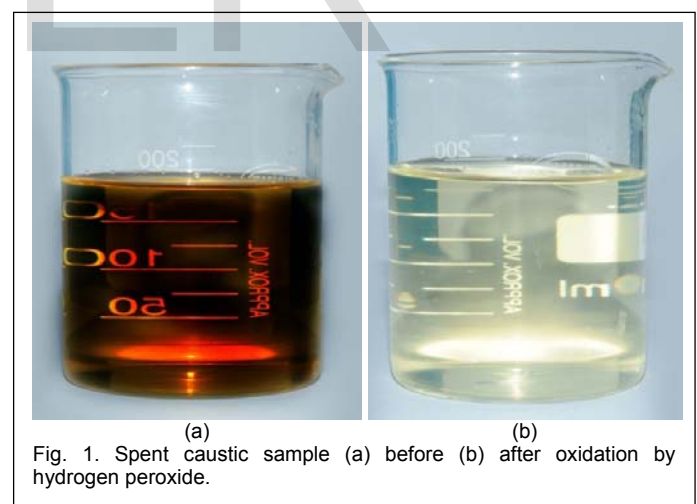


Fig. 1. Spent caustic sample (a) before (b) after oxidation by hydrogen peroxide.

After oxidation, spent caustic sample was treated by 50 mL of sulfuric acid within a batch reactor based on analysis results. Treatment process was performed at different temperatures and samples were taken at short sampling time periods for analysis.

2.1 Experimental Design

In this work central composite design (CCD) method [21] was used for design of experiments. Two main factors of initial spent caustic temperature and sampling time were used as input variables in order to assess their effect on spent caustic

removal. 15 experiments with one repeat at the center were proposed by MINITAB® software. The ranges of input variables are shown in Table 3. Also design matrix is shown in Table 4.

TABLE 3
SUGGESTED INPUT VARIABLES AND THEIR VALUES FOR EXPERIMENTAL DESIGN

Input variables	Values
Initial temperature (°C)	25, 35, 45
Sampling time (min)	0.5, 1, 1.5, 2, 2.5

TABLE 4
DESIGN MATRIX FOR THE EXPERIMENTS

Experiment number	Initial temperature (°C)	Sampling time (min)
1	25	0.5
2	35	0.5
3	45	0.5
4	25	1
5	35	1
6	45	1
7	25	1.5
8	35	1.5
9	45	1.5
10	25	2
11	35	2
12	45	2
13	25	2.5
14	35	2.5
15	45	2.5

2.2 Analysis methods

2.2.1 Measurement of carbonate ion and caustic

For measurement of these two bases, HCl is gradually added to the treated solution and profile of pH was depicted. Two picks are observed in pH curve where the first pick is for carbonate ion and the other for sodium hydroxide. Using volume of acid consumed for reaching each pH, concentrations of carbonate ion and caustic can be calculated [22].

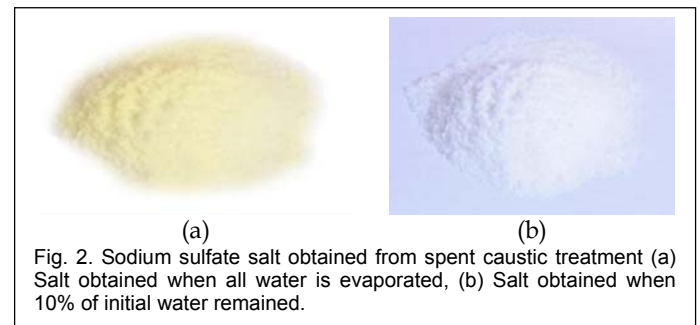
2.2.2 Measurement of sulfate ion

For measurement of sulfate ion in the samples, Palintest® device was used. The method is that 10 mL of the sample is passed through a filter in order to remove its opacity. Then it is decanted in test tube of the device and a tablet specific for sulfate ion is located in tube and completely stirred to dissolve the tablet. After calibration of the device, the amount of sulfate ion is read.

2.3 Separation of sodium sulfate

After completion of the reactions, the remaining solution must be placed within an oven in order to evaporate its water content. If water content of spent caustic is completely evaporated, the color of sodium sulfate will become light yellow, because of its impurities (Fig. 2 (a)). But if sodium sulfate is gradually gathered from the bottom of the vessel when there exists 10% of initial water content, sodium sulfate

color will be white, because solubility of most impurities is higher than sodium sulfate (Fig. 2 (b)).



3 RESULTS AND DISCUSSION

Fig. 3 shows changes in color and phenol content of spent caustic for 30 minutes. As can be seen, color of the solution reduces sharply because of generation of hydroxide ions. Also phenol content reduces largely. Fig. 4 shows concentration changes of hydroxide, thiosulfate, carbonate and sulfate ions and pH of the treated waste with respect to time. As can be seen, concentration of ions reduces with time and they are converted to sodium sulfate according to Eqs. 1 to 6. Before treatment, pH of the solution is basic (pH=13.3), while after adding sulfuric acid it reduces sharply and reaches to about 2. Maximum conversion of the waste to sodium sulfate was about 89%.

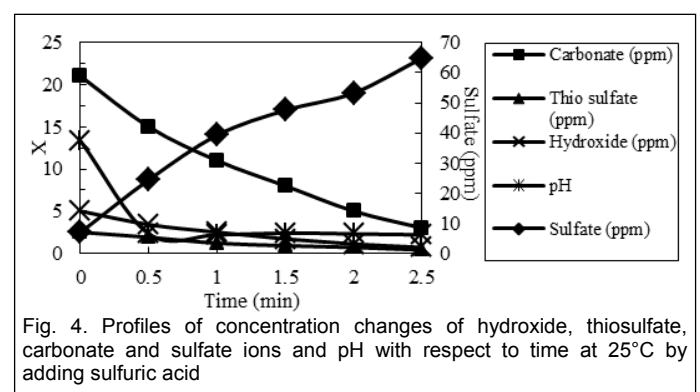
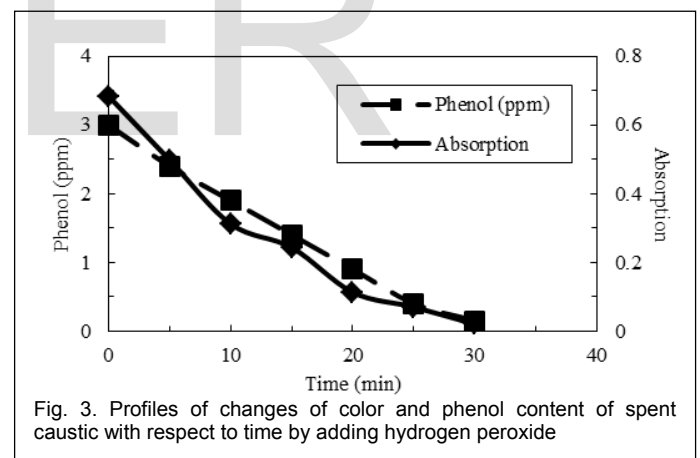


Fig. 4. Profiles of concentration changes of hydroxide, thiosulfate, carbonate and sulfate ions and pH with respect to time at 25°C by adding sulfuric acid

An empirical model was obtained based on experimental results to represent process response which is percent conversion of spent caustic pollutants ($R\%$) with respect to initial temperature (T in $^{\circ}\text{C}$) and reaction time (t in min) using linear regression:

$$R\% = 10.052 + 22.774t + 1.208T - 0.252T \times t \quad (8)$$

The experimental and modeling results are shown in Table 5. Coefficient of determination, R^2 , is 0.9758 which indicates that 97.58% of the changes in the response are predicted by proposed model.

TABLE 5

COMPARISON OF EXPERIMENTAL RESULTS WITH THE RESULTS OBTAINED BY RSM MODEL

Experiment number	Initial temperature ($^{\circ}\text{C}$)	Reaction time (min)	Conversion (%)	
			Experimental	RSM
1	25	0.5	46.62	48.49
2	35	0.5	57.36	59.31
3	45	0.5	69.26	70.12
4	25	1	56.17	56.73
5	35	1	68.83	66.29
6	45	1	77.14	75.85
7	25	1.5	68.82	64.96
8	35	1.5	72.77	73.27
9	45	1.5	80.24	81.57
10	25	2	74.64	73.20
11	35	2	81.36	80.25
12	45	2	89.53	87.29
13	25	2.5	79.36	81.44
14	35	2.5	84.44	87.23
15	45	2.5	92.45	93.01

The following diagrams are plotted using MINITAB[®]. Fig. 5 shows normal distribution curve and values of residuals obtained by the model.

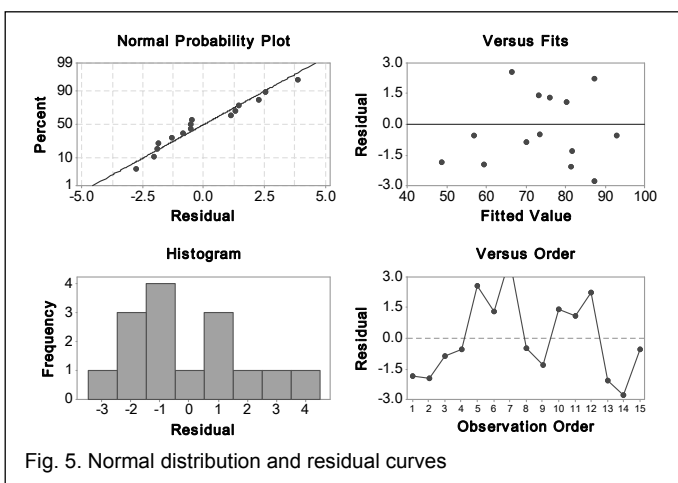


Fig. 5. Normal distribution and residual curves

As can be seen, linearity of normal distribution curve and randomness of residuals distribution represents correctness of the model. Noting obtained results, it can be concluded that

the proposed model predicts experimental results with an acceptable accuracy and can be used for prediction of output variable in other conditions within the range of input variables. The proposed model was used for analysis of variance in order to calculate degrees of freedom, sum and mean square of errors, F-statistics, and P value for each factor (Table 6). According to F and P values in Table 6, the most effective parameters on removal efficiency of spent caustic are initial temperature, reaction time, and temperature*reaction time, respectively.

TABLE 6

ANALYSIS OF VARIANCE FOR REMOVAL EFFICIENCY

Source of change	Degree of freedom	Adj. SSE*	Adj. MSE**	F statistics	P value
Temperature	1	265.233	265.233	53.94	0.000
Reaction time	1	200.764	200.764	40.83	0.000
Temperature*	1	31.702	31.702	6.45	0.028
Reaction time					
Error	11	54.09	4.917		
Sum	14	2236.61			
R^2		0.9758			

* Adjusted Sum of Squared Errors

** Adjusted Mean of Squared Errors

Fig. 6 shows the effect of interaction between main factors on removal efficiency. Also Fig. 7 shows optimum region for performing treatment process.

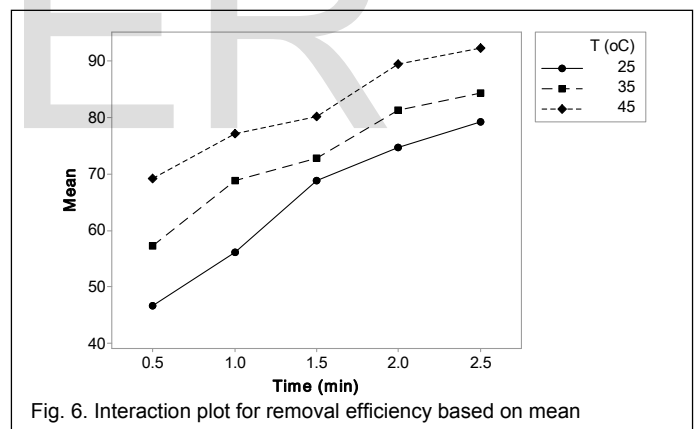


Fig. 6. Interaction plot for removal efficiency based on mean

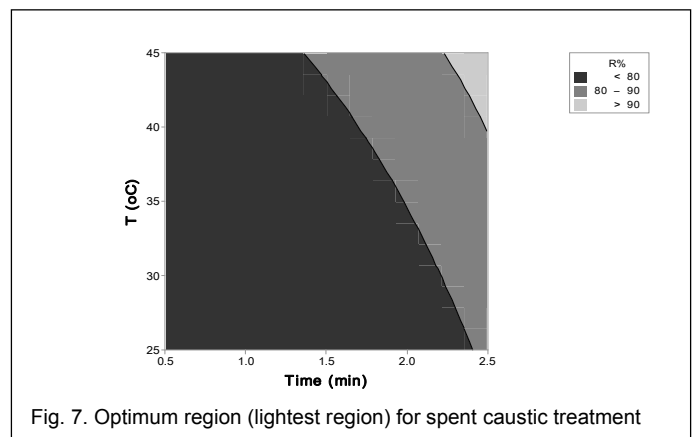


Fig. 7. Optimum region (lightest region) for spent caustic treatment

4 CONCLUSION

In this work, a new method was proposed and used for treatment of spent caustic pollutant, so instead of waste disposal it is converted to a solution containing only sodium sulfate using sulfuric acid without large operating costs. Results of oxidation with hydrogen peroxide showed that color and phenol content of spent caustic decreased sharply in 30 minutes.

For the assessment of the effect of initial temperature and reaction time on treatment efficiency, experimental design methodology was applied. Results of experiments showed that initial temperature has greatest effect on removal efficiency. Based on the results, the best initial temperature for treatment is 45°C which is the maximum value used for the experiments and temperatures greater than this value must be assessed. The best reaction time at this temperature is 2 minutes, because at this time pH of the solution is neutral and after that the solution becomes acidic.

Because sulfuric acid price is lower than hydrochloric acid, by using this method not only operating costs are reduced, but also a valuable product, i.e. sodium sulfate, is produced and also pH of the solution is set in neutral region. The other advantage of this method is that it can be performed at moderate temperatures and at atmospheric pressure with good reaction rate.

5 ACKNOWLEDGMENT

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