Petroleum Research

Petroleum Research 2018 (December-January), Vol. 28, No. 102. 29-32

DOI: 10.22078/pr.2018.3292.2520

Sulfide ion removal from sodium hydroxide solution by ozonation/adsorption method

Jamshid Behin

Faculty of Petroleum and Chemical Engineering, Razi University, Kermanshah, Iran

Behin@razi.ac.ir

Doi: 10.22078/pr.2018.3292.2520

Received: May/18/2018 Accepted: August/26/2018

INTRODUCTION

Nowadays, reutilization of flare gas is receiving much more consideration due to high energy content. Hydrogen sulfide (H_2S), as a corrosive-acidic gas, is one of the main pollutants in the flare gas in oil refineries and petrochemical companies. The reutilization will be a feasible route if this constituent separated perfectly from the main gas stream. Although amines are the conventional solvents; however they aren't an economical solvent for this purpose. In comparison to different chemicals, sodium hydroxide (NaOH) is an efficient cost effective solvent and there is no hazardous residual for environment if it is regenerated properly [1]. While NaOH brings in contact with an acidic gas such as flare gas containing H_2S, mercaptanes and other sulfur compounds, an alkaline wastewater called caustic (pH≥12) is generated. Biological, oxidation and membrane technologies are the different methods for the caustic regeneration, among them air-oxidation is more popular [2,3]. In this method, sulfur compounds were oxidized to thiosulfate, sulfite and sulfate ions; then they were removed from solution with precipitation [4], electro-cogulation [5], crystallization [6] and adsorption [7]. In the present work and for the first time, advanced oxidation with ozone followed by adsorption on natural zeolite (clinoptilolite) was applied to oxidized sulfide to sulfate ions and to remove them from caustic solution (at constant pH) for the regeneration purpose.

MATERIALS AND METHODS

The ozonation experiments were conducted in Pyrex bubble column rector of 1.5 L in volume.

A synthetic alkaline solution containing NaOH (0.003 M) was prepared. In each experimental run, desired amount of Na_2S and H_2O_2 were added. The H_2O_2 improves the oxidation reaction and generates high reactive OH° radicals. Ozone was generated from air in an ozone generator (Arda/France). The set-up scheme is illustrated in Figure 1.

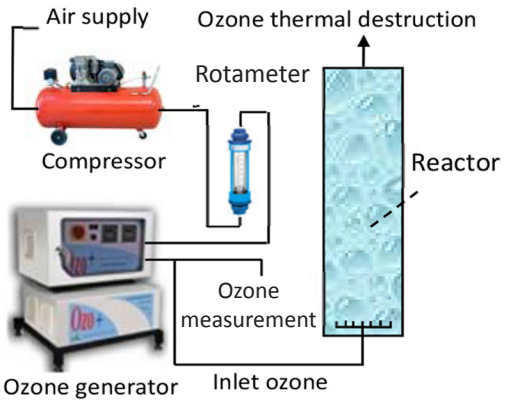

Figure 1: Experimental ozonation set-up

The samples were taken for further analysis after desired time intervals. The UV-VIS spectrophotometer (Hanon/China) was used to measure the concentration of sulfate ions. The removal efficiency was determined from initial (C_o) and final (C_t) sulfide concentration using following relation:

$$\eta(\%) = 1 - C_t / C_o \quad (1)$$

Design of experiment was executed using Design Expert software (7.0.0). Response surface method (RSM) based on central composite design (CCD) was applied to analysis the influence of operating variables, i.e., ozonation time, Na_2S concentration and volume of H_2O_2 as well as to find the optimal response factor. The software suggested 17 experiments based on independent variables at three levels. The optimum ozonation condition, considering the highest conversion of sulfide ions to sulfate, was selected for further adsorption experiments.

The adsorption experiments were conducted on natural and modified zeolite.

The natural clinoptilolite (Semnan/Iran) was added to NaCl solution to remove its impurities and to exchange Na^+ cation. After washing and overnight drying, the solid was suspended to $BaCl_2$ solution to exchange Ba^{2+} with Na^+. The modified clinoptilolite was washed and dried for adsorption experiments. The adsorption experiments were conducted using single variable at the time with various dose of zeolite (W/V). The adsorption capacity was calculated using the following relation [8,9]:

$$q = (C_o - C_t)(V / W) \quad (2)$$

RESULTS AND DISCUSSION

The model was applied to obtained experimental data. The ANOVA results showed that the model was significant. The quadratic relation based on significant un-coded variables was suggested as:

$$\eta\ (\%) = -8.851 + 0.456\ V_{H_2O_2} + 221\ [Na_2S] + 0.041\ t\ V_{H_2O_2} + 0.008\ t^2 \quad (3)$$

The effect of influent variables was in the following order:

$$\text{Ozonation time} > V_{H_2O_2} > [Na_2S]$$

The actual and predicted values were closed indicating the modelis suitable. The interaction of variables is shown in Figure 2. The ozonation time and volume of H_2O_2 have more simultaneous effect on removal efficiency.

The optimum experimental condition for ozonation reaction was obtained as: Na_2S concentration: 0.03 M, H_2O_2 volume: 5 mL and ozonation time: 60 min. under this condition, the conversion efficiency was obtained 72.11%.

The results of adsorption experiments are shown in Table 1. The highest adsorption efficiency 91% was obtained with modified clinoptilolite at the highest dosing level 8 g/100 mL solution.

An increase in the adsorbent dosage resulted in an increase the surface area as well as available active sites. The results of adsorption experiments are shown in Table 1. The highest adsorption efficiency 91% was obtained with modified clinoptilolite at the highest dosing level 8 g/100 mL solution.

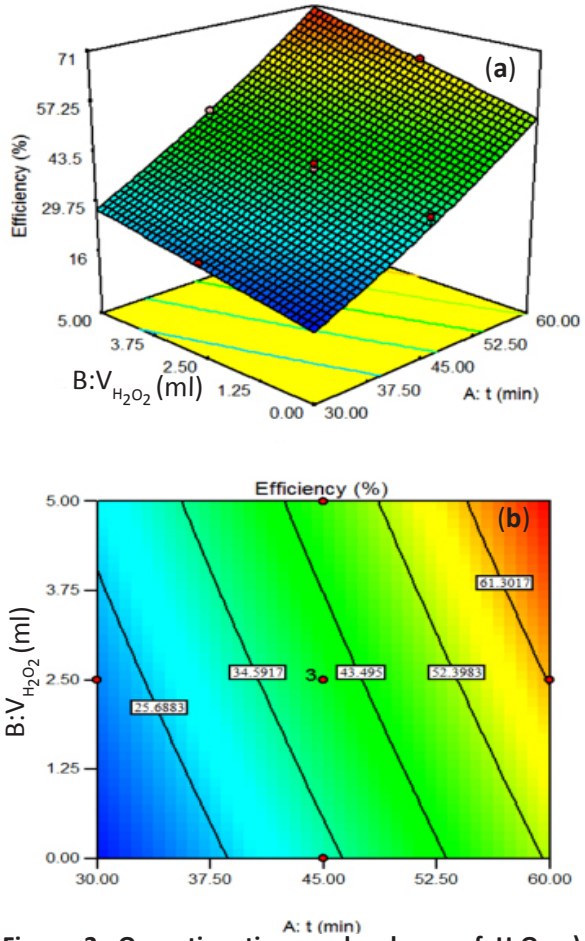

Figure 2: Ozonation time and volume of H_2O_2 a) three-dimension b) two-dimension.

Table 1. Adsorption efficiency of sulfate ions on natural and modified clinoptilolite.

Adsorbent dose	Adsorption efficiency (%)	
g	Natural clino	Modified clino
1	15.03	54.92
2	18.97	59.89
3	21.93	67.13
4	27.11	72.08
5	34.01	79.52
6	35.95	84.49
7	37.00	87.05
8	34.18	90.91

An increase in the adsorbentdosage resulted in an increase the surface area as well as available active sites. Non-linear form of Langmuir and Ferundlich adsorption isotherms were fitted to experimental data at ambient temperature (25 °C) and isotherm parameters were determined using nonlinear regression. High correlation coefficient indicated that Langmuir isotherm was well fit to the experimental data that is in an agreement with literature. Kinetic study was also performed and pseudo first and second order constants were obtained. The following process flow diagram was suggested for sulfur removal from flare gas (Figure 3).

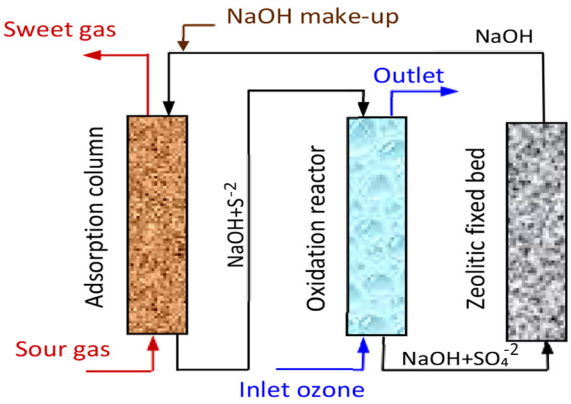

Figure 3: Suggested process flow diagram for sulfur removal from flare gas.

CONCLUSIONS

The regeneration of spent caustic with ozone was investigated for conversion of sulfide to sulfate ions in a bubble column reactor followed by adsorption on zeolitic surface. The conversion efficiency 72.2% was obtained under the optimum condition of oxidation experiment. The adsorption with modified Ba-clinoptilolite resulted in 91% removal of sulfate ions from solution. Therefore, the total removal efficiency 65.7% was achieved for ozonation-adsorption combination process. Although, the obtained removal efficiency was comparable with other methods such as electro-cogulation; however no H_2S gas was released in the suggested method.

REFERENCES

[1]. Suarez F. J., *"Pluses and minuses of caustic treating,"* Hydrocarbon Processing, Vol. 75, pp. 117-123, 2006.

[2]. Keramati N., Moheb A. and Ehsani M. R., *"Effect of operating parameters on NaOH recovery from waste stream of Merox tower using membrane systems: Electrodialysis and electrodeionization processes,"* Desalination, Vol. 259, pp. 97-102, 2010.

[3] Ellis C.E., "*Wet air oxidation of refinery spent caustic*", Environmental Progress, Vol. 17, pp. 28-30., 1988.

[4]. Benatti C., *"Sulfate removal from waste chemicals by precipitation,"* Journal of Environmental Management, Vol. 90, pp. 504-511, 2009.

[5]. Yousuf M., *"Electrocoagulation (EC)-science and applications,"* Journal of Hazardous Materials B, Vol. 84, pp. 29-41, 2001.

[6]. Tait S., *"Removal of sulfate from high-strength wastewater by crystallization,"* Water Research, Vol. 43, pp. 762-772, 2009.

[7]. Namasivayam C. and Sangeetha D., *"Application of coconut coir pith for the removal of sulfate and other anions from water,"* Desalination, Vol. 219, pp. 1-13, 2008.

[8]. Faghihian H. and Kazemian H., *"Ion exchange of Pb^{+2}, Ag^{+}, Ni^{+2} and Zn^{+2} in natural clinoptilolite, study of some parameters,"* Iranian Journal of Science and Technology, Vol. 26, pp. 357-361, 2002.

[9]. Menhaje Bena R., Kazemian H., Ghazi-Khonsari M., Hosseini M. and Shahtaheri S. J., *"Evaluation of some Iranian natural zeolites and their relevant synthetic zeolites as sorbents for removal of arsenate from drinking water,"* Iranian Journal of Public Health, Vol. 33, pp. 36-44, 2004.