Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/petroleum-coal
Petroleum & Coal 56(5) 503-508, 2014

EFFECTIVE REMOVAL OF H_2S USING POLYETHYLENE POLYAMINE LOADING ATTAPULGITE

Xinpeng Liu, Rui Wang*

*School of Environmental Science and Engineering, Shandong University, No. 27 Shanda South Road, Jinan 250199, P. R. China.*Email: ree_wong@hotmail.com*

Received June 19, 2014, Accepted October 6, 2014

Abstract

Polyethylene Polyamine (HPAX) loading attapulgite has been prepared successfully as a H_2S sorbent at low temperature. The effect of prehumidification, temperature, H_2S concentration and HPAX loading were investigated. The sorbent showed a highest breakthrough sulfur capacity of 2.55 mg/g-sorbent and a saturation sulfur capacity of 3.12 mg/g-sorbent at 25°C. Prehumidification, decrease of temperature, lower flow rate and H_2S concentration were in favor of sorption of H_2S. The best conditions were as follows: the prehumidification time was 1 h, the temperature was 25 °C, the HPAX loading was 33.3%.

Key words: attapulgite; polyethylene polyamine; H_2S; sorption.

1. Introduction

Hydrogen sulfide (H_2S) is a common toxic, corrosive and smelly gas which present in fuel gases such as natural gas, syngas and biogas. The existence of H_2S in fuel gases will result in corrosion of pipelines and poisoning of catalysts even at a low concentration [1]. What's more, H_2S has a negative impact on human's neural system and important organs such as kidney and liver [2]. The removal of H_2S has been an important task for many researchers.

The removal of H_2S could be realized by the absorption of liquid solution or adsorption of solid sorbents. Adsorption/oxidation of H_2S by porous materials has been appreciated by more and more researchers because of their higher energy efficiency, easier regeneration and higher desulfuration capacity [3]. Activated carbon has been used for the removal of H_2S widely due to the unique pore structure and surface property. Elemental sulfur and sulfuric acid are the main products of the oxidation taking place on the surface of activated carbon [4-7]. Metal oxides [1, 8], molecular sieve [9], carbon nanotubes [10] and Metal- Organic Frameworks (MOFs) [11-12] *et al.* are also used as sorbents for H_2S removal.

Amine-loading could enhance the adsorption capacity of porous materials for H_2S removal and improve H_2S selectivity through an acid-base interaction at a low temperature. Numerous reports on loading $-NH_2$ groups to the surface of porous materials have been published [9, 13-14]. Song *et al.* [15-17] developed a series of sorbents for acid gas removing called "molecular basket" which showed perfect performance by loading polyethylenimine (PEI) on the mesoporous molecular sieve. Chen *et al.* [18] developed a H_2S sorbent which demonstrated a large H_2S breakthrough capacity of 1.27 mmol of H_2S/ (g of sorbent) at 22°C by loading

PEI on hierarchical porous silica monolith. However, most reports focused on the porous materials synthetized from bench-scale study. The object of this article is to develop an amine-loading sorbent by loading Polyethylene Polyamine (HPAX) on the surface of attapulgite (ATTP), a common porous mineral.

2. Materials and methods

2.1. Materials

Polyethylene Polyamine (HPAX, nitrogen content: 32-35%) was bought from Tianjin Kermel chemical reagent co., ltd., China; Ethanol absolute (purity ≥ 99.5%) was purchased from Tianjin Fuyu fine chemistry co., ltd., China; Attapulgite (ATTP) was purchased from Jinan Chenyang chemical sales department, China. All above chemical were used as received.

2.2. Methods

2.2.1. Preparation of the sorbent for H_2S removal

In a typical preparation, the desired amount of HPAX was dissolved into 50 mL ethanol absolute at room temperature under stirring for 30 min, and then 5 g ATTP was added to the above solution and refluxed for 2 h at 80°C. Next, the slurry was maintained at 80°C to evaporate the solvent and dried at 100 °C for 1 h to obtain the powder, then the sorbent was obtained by tableting and grinding to the size of 0.25-0.42 mm. The as-preparation sorbent was denoted as ATTP-xHPAX, where x represents the weight percentage of HPAX in the sorbent (ATTP + HPAX). Before sorption test, all the sorbents were pretreated at 100°C under a nitrogen (99.999%) flow at 200 mL/min for 2 h and prehumidified at room temperature under a moist (80%) nitrogen flow of 200 mL/min for 1 h.

2.2.2. H_2S Sorption Measurement

The sorption tests were carried out using a glass tube with inner diameter of 12 mm and height of 20 cm in which 2.0 g of the sorbent was packed (the length of sorbent layer was 50mm) to evaluate the capacity of the as-preparation sorbent for H_2S removal. The temperature of adsorption was controlled by a Yuhua DH-101S thermostat water bath. A mixture gas (nitrogen as the carrier gas) containing 420 mg/m^3 of H_2S was passed through the column of sorbent at a flow rate of 200 mL/min. The H_2S concentration of the outlet gas was detected by a TH-990s hydrogen sulfide gas analyzer (every five minutes to read a number of time). The residual exhaust gas was adsorbed by NaOH solution. When the outlet H_2S concentration reached to the initial concentration i.e. the sorbent was saturated by H_2S, the test was stopped. In this test, the breakthrough concentration of H_2S was defined as 10% of the initial concentration. The breakthrough and saturation sulfur capacities of the sorbents were calculated by integration of the areas above the breakthrough curves (time as the x-coordinate, the ratio of measured and initial concentration as the y-coordinate), and from the flow rate, H_2S initial concentration, breakthrough and saturation time and mass of the sorbent. The breakthrough and saturation sulfur capacities are denoted as Cap (B) and Cap (S), respectively.

3. Results and discussion

3.1. Effect of prehumidification time

The effect of prehumidification time on H_2S sorption performance of the sorbent has been investigated, as shown in Fig. 1. It was obviously that the H_2S sorption performance of the sorbent prehumidified was superior to that without prehumidification. At the beginning of sorption, H_2S was adsorbed completely and unable to be detected. The sorbent prehumidified for 1.5 h showed a better H_2S sorption than that prehumidified for 0.5 h, but no better than that prehumidified for 1 h. This indicated that the effect of water reached the highest point with prehumidification for 1 h. There are several possible reasons to explain the effect of prehumidification. Wang *et al.* [15] thought that the presence of water might change the chemical interaction of H_2S and amine groups and then each amine groups molecule could react with more H_2S molecules, or H_2S might be adsorbed by water itself. Seredych *et al.* [6] thought that water likely played a role in the H_2S retention on the surface of sorbent.

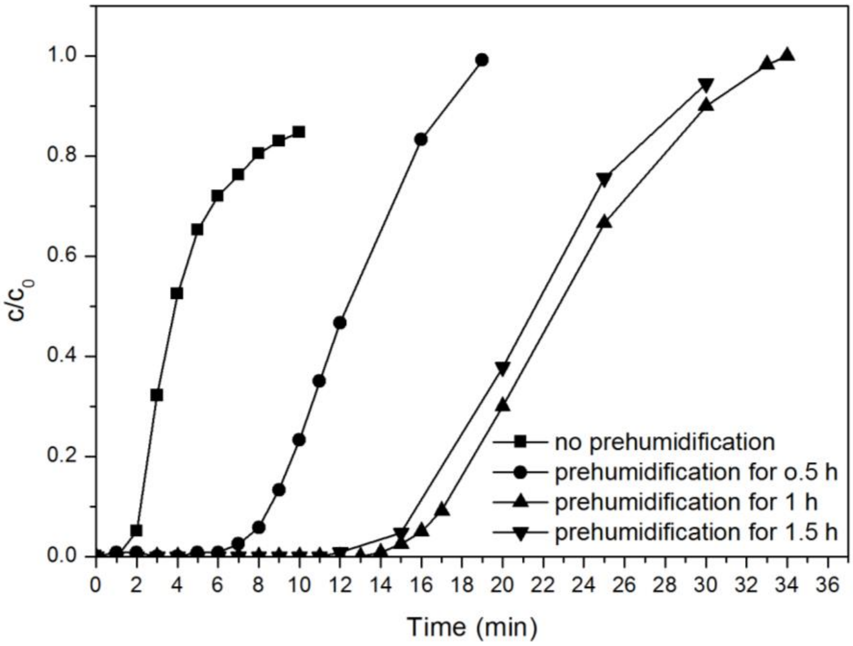

Fig. 1. Breakthrough curves of H_2S on ATTP-16.7HPAX with different prehumidification time (25°C)

3.2. Effect of temperature

The breakthrough curves of H_2S on ATTP-16.7HPAX at different sorption temperatures (25, 35 and 50°C) are shown in Fig. 2. The corresponding sorption capacities are listed in Table 1. It was clearly that with the increase of the sorption temperature, both the breakthrough and saturation sulfur capacities decreased significantly. The breakthrough and saturation sulfur capacities at 25°C were 0.35 and 0.50 mg-sulfur/g-sorbent respectively, showing a superior effect compared with those at either 35 or 50°C.

The results showed that lower temperature favors H_2S sorption, despite a higher temperature could enhance the kinetic diffusion of H_2S on the surface of sorbent. This may be controlled predominantly by the weak thermodynamic stability of bonds between H2S molecules and amine groups [18]. H_2S is weak acid and the bonds formed with amine groups are so weak that they would break easily at a high temperature. On the other hand, the transfer of adsorbed H_2S on the surface into the HPAX bulk inside pores may be easily at room temperature because of the lower kinetic barrier [16].

Table 1. Sulfur sorption capacities of ATTP-16.7HPAX at different temperature

Temperature (°C)	Cap (B) (mg/g-sorbent)	Cap (S) (mg/g-sorbent)
25	0.35	0.50
35	0.16	0.27
50	0.12	0.17

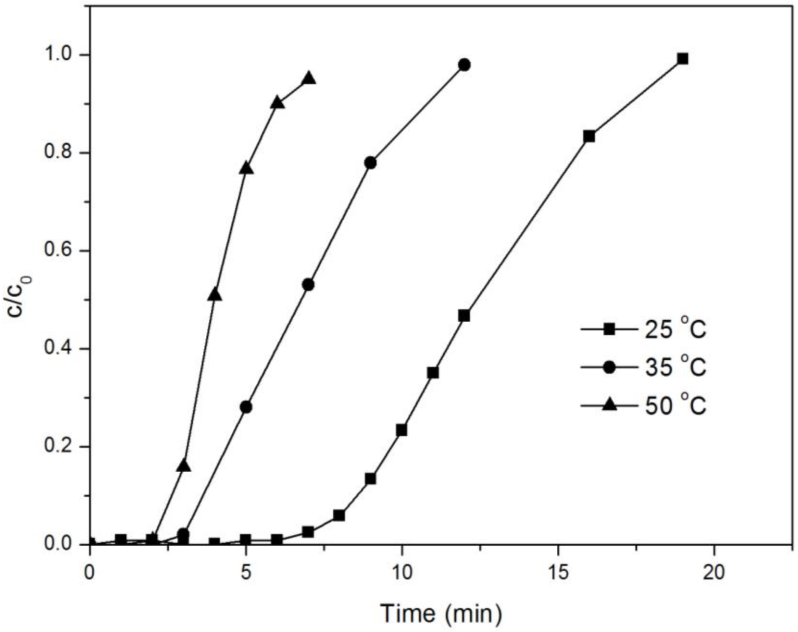

Fig. 2. Breakthrough curves of H_2S on ATTP-16.7HPAX at different temperatures

3.3. Effect of H_2S concentration

The effect of H_2S concentration on H_2S sorption performance of the sorbent has been investigated, as shown in Fig. 3. The breakthrough and saturation times of sorbent under a concentration of 455 mg/m^3 are nearly twice as those under a concentration of 770 mg/m^3. However, the flow rates of both the concentrations are the same. The breakthrough and saturation sulfur capacities of the sorbents under 455 and 770 mg/m^3 at 100 mL/min are 0.74 and 1.05 mg/g, 0.73 and 0.99 mg/g, respectively, slightly better than that under the flow of 200 mL/min, 420 mg/m^3 (0.63 and 0.91 mg/g). The results indicated that lower flow rate and lower H_2S concentration have a favorable effect on the sulfur capacity of sorbent.

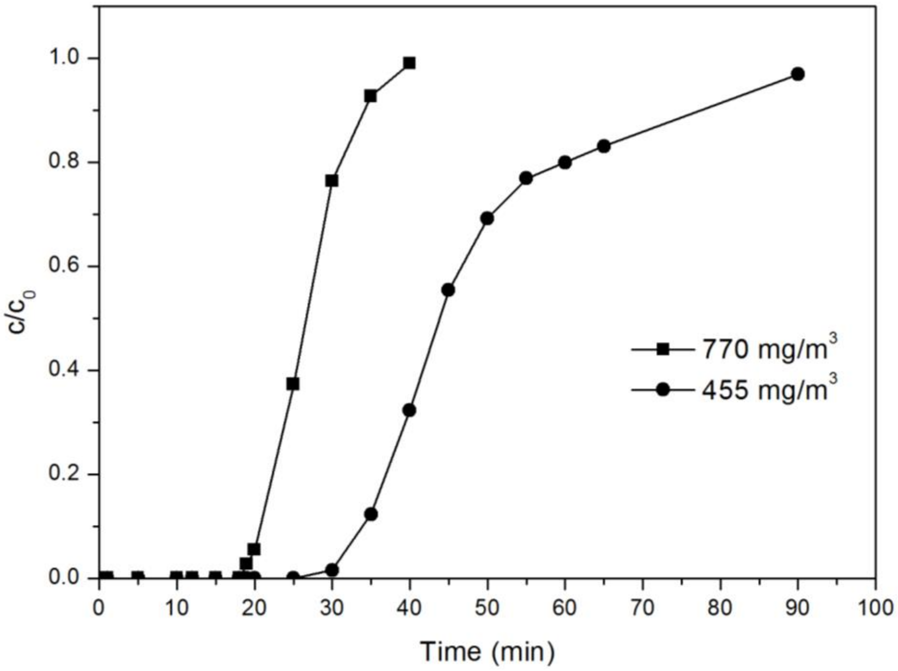

Fig. 3. Breakthrough curves of H_2S on ATTP-16.7HPAX under different H_2S concentrations (flow rate: 100 mL/min, 25°C)

3.4. Effect of HPAX loading

The effect of HPAX loading on the desulfurization performance of sorbent is shown in Fig. 4. The breakthrough curves of H2S on sorbents with different HPAX loading is shown in Fig. 4.a. ATTP alone showed a poor breakthrough sulfur capacity (0 mg/g) and saturation sulfur capacity (0.08 mg/g) which might be caused by physisorption, so the sorption of H_2S on HPAX loading sorbents should be mainly chemisorption. As shown in Fig. 4.b, the breakthrough and saturation sulfur capacities increased when the HPAX loading increased from 0 to 33.3%, and then, decreased with the HPAX loading increased continuously. The breakthrough and saturation sulfur capacities both reached at the maximum point at the loading of 33.3%, and the corresponding capacities were 2.55, 3.12 mg/g, respectively.

The sulfur sorption capacity increased at the beginning on account of the increase of amine groups on the surface. HPAX should disperse well when the loading was low, so the amount of amine groups would increase with the increase of HPAX loading. However, the porosity was blocked by excessive loading of HPAX when the HPAX loading surpassed 33.3%, and then most HPAX could not be used because of the long distance of H_2S from the surface into the internal HPAX [18].

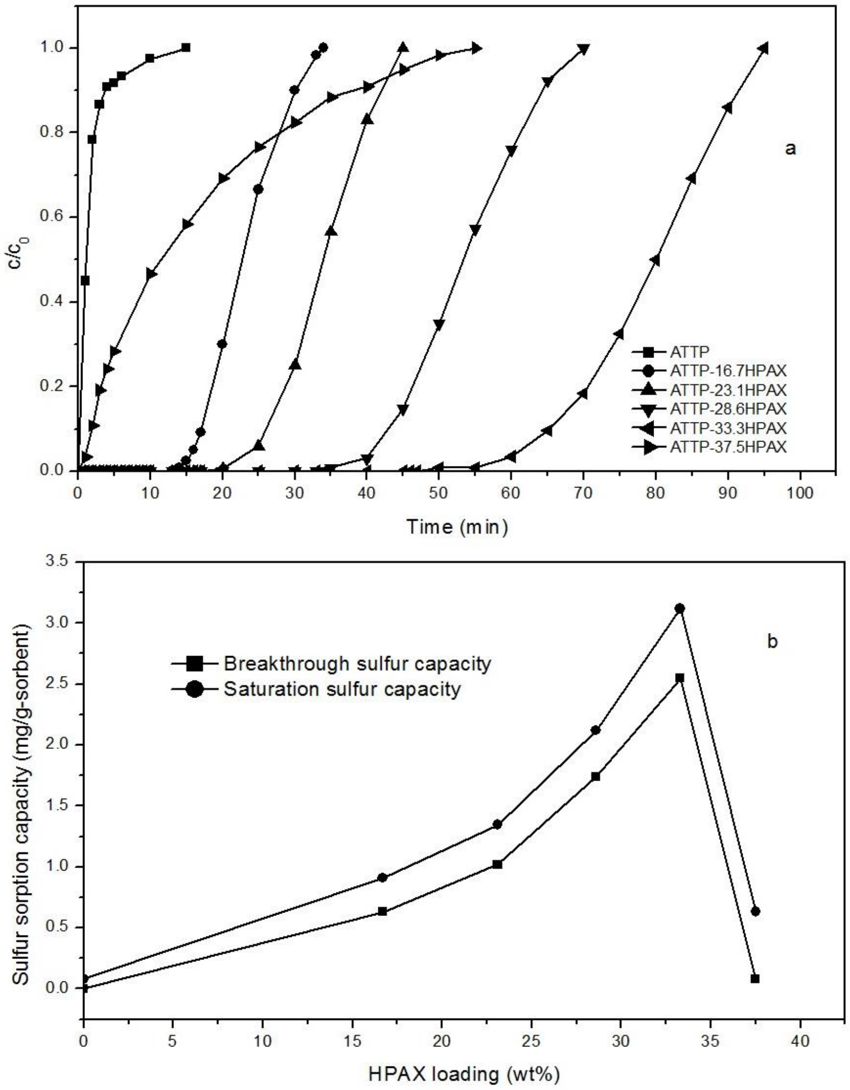

Fig. 4. Effect of HPAX loading on the desulfuration performance of sorbent (25°C): a, breakthrough curves of H_2S on sorbents with different HPAX loading; b, breakthrough and saturation sulfur capacities of sorbents with different HPAX loading

4. Conclusions

In this research, a series of HPAX-loading sorbents were successfully prepared and used in sorption of H_2S. The result has shown that HPAX-loading sorbent could effectively remove H_2S at ambient conditions. It is found that the prehumidification and low temperature favor enhancing the sorption capacity of supported HPAX sorbents. The HPAX loading has a strong influence on the performance of the sorbents. The best loading was 33.3%, with which the sorbent has a highest breakthrough sulfur capacity of 2.55 mg/g-sorbent and saturation sulfur capacity of 3.12 mg/g-sorbent at 25°C. Considering the relative lower sorption capacity compared with the sorbent which prepared by molecule sieve, more research about cheap and accessible porous support materials should be done.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21276144), the Scientific Key Project from Chinese Ministry of Education (No. 109094), and the Ph. D. Program Project for Priority Development Field from Chinese Ministry of Education (No. 20110131130001).

References

[1] Rezaei, S.; Tavana, A.; Sawada, J. A.; Wu, L.; Junaid, A. S.; Kuznicki, S. M.: Ind. Eng. Chem. Res. 2012, 51, 12430.

[2] Feng, W. G.; Kwon, S.; Borguet, E.; Vidic, R.: Environ. Sci. Technol. 2005, 39(24), 9744.

[3] Belmabkhout, Y.; Weireld, G. D.; Sayari, A.: Langmuir, 2009, 25(23), 13275.

[4] Bagreev, A.; Rahman, H.; Bandosz, T. J.: Ind. Eng. Chem. Res. 2000, 39(10), 3849.

[5] Yan, R.; Chin, T.; Ng, Y. L.; Duan, H. Q.; Liang, D. T.; Tay, J. H.: Environ. Sci. Technol. 2004, 38(1), 316.

[6] Seredych, M.; Bandosz, T. J.: Energy & Fuels, 2008, 22(2), 850.

[7] Chen, Q. Y.; Wang, Z.; Long, D. H.; Liu, X. J.; Zhan, L.; Liang, X. Y.; Qiao, W. M.; Ling, L. C.: Ind. Eng. Chem. Res. 2010, 49(7), 3152.

[8] Fan, H. L.; Sun, T.; Zhao, Y. P.; Guan, J. S.; Lin, J. Y.: Environ. Sci. Technol. 2013, 47, 4859.

[9] Chu, X. Z.; Cheng, Z. P.; Zhao, Y. J.; Xu, J. M.; Zhong, H.; Zhang, W. G.; Lu, J. S.; Zhou, S. Y.; Zhu, F. X.; Zhou, Y. P.; Zhou, L.: Ind. Eng. Chem. Res. 2012, 51, 4407.

[10] Mohamadalizadeh, A.; Towfighi, J.; Rashidi, A.; Mohajeri, A.; Golkar, M.: Ind. Eng. Chem. Res. 2011, 50, 8050.

[11] Hamon, L.; Serre, C.; Devic, T.; Loiseau, T.; Millange, F.; Ferey G.; Weireld, G. D.: J. AM. CHEM. SOC. 2009, 131(25), 8775.

[12] Gutierrez-Sevillano, J. J.; Martin-Calvo, A.; Dubbeldam, D.; Calero, S.; Hamad, S.: RSC Advances, 2013, 3, 14737.

[13] Huang, H. Y.; Yang, R. T.; Chinn, D.; Munson, C. L.: Ind. Eng. Chem. Res. 2003, 42(12), 2427.

[14] Belmabkhout, Y.; Heymans, N.; Weireld, G. D.; Sayari, A.: Energy & Fuels, 2011, 25, 1310.

[15] Wang, X. X.; Ma, X. L.; Sun, L.; Song, C. S.: Green Chemistry, 2007, 9, 695.

[16] Wang, X. X.; Ma, X. L.; Xu, X. C.; Sun, L.; Song, C. S.: Top Catal, 2008, 49, 108.

[17] Ma, X. L.; Wang, X. X.; Song, C. S.: J. AM. CHEM. SOC. 2009, 131(16), 5777.

[18] Chen, Q. J.; Fan, F. C.; Long, D. H.; Liu, X. J.; Liang, X. Y.; Qiao, W. M.; Ling, L. C.: Ind. Eng. Chem. Res. 2010, 49(22), 11408.