Removal of hydrogen sulfide on activated carbon supported ionic liquids

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Abstract. In this study, ionic liquid loaded activated carbon was applied as the adsorbent for hydrogen sulfide (H2S) removal under the anaerobic conditions in a fixed bed. The effects of activated carbon substrate, ionic liquid, initial H2S concentration and flow rate on the adsorption process were systematically studied. The experimental results show that the activated carbon named AC-1 having higher surface area and micropore volume is more suitable as the support for ionic liquid. Amongst three ionic liquids studied, the 1-ethyl-3-methylimidazolium acetate loaded activated carbon exhibites the highest H2S sorption capacity performance. As a results of the superior performance of the 1-ethyl-3-methylimidazolium acetate loaded activated carbon, further tests and characterizations were performed on the sorbent. The breakthrough capacity of 1-ethyl-3-methylimidazolium acetate sorbent is two times greater than pure activated carbon. In addition, it is confirmed that increasing H2S concentration enhances H2S adsorption capacity, and the adsorption capacity of H2S decreases significantly with increasing gas flow rate.

1. Introduction

Hydrogen sulfide (H2S) is one of the common malodorous compounds that can be found in petroleum deposits, natural gas, volcanic gases and emissions from many industrial plants [1]. Removal of H2S is an important issue owing to not only its harmful effects on the environment and health but also to its tendency to poison catalysts used in various chemical processes [2-4].

Conventional removal methods for H2S include wet scrubbing, adsorption, biological methods and catalytic oxidation. Wet scrubbing uses basic chemicals such as amine solution and alkali solution, because H2S is an acidic gas [5, 6]. Meikap et al. [7] studied the performance of a lab-scale three stage dual-flow sieve plate column scrubber for H2S removal from a gas stream. Adsorption by an adsorbent, such as activated carbon, silica gels, zeolites and alumina is able to trap H2S in its porous structure [8, 9]. Biological methods use some kinds of bacteria to consume H2S for growth [10]. Catalytic oxidation uses some special catalyst to convert H2S into elemental Sulphur [11-13]. Among these methods mentioned above, adsorption by activated carbons is considered as an efficient and economical approach [14-17].

As a green nonvolatile solvent which has attracted the attention of many researchers, ionic liquid (IL) has been used for acidic gas removal [6, 18-22], such as H2S, CO2 and SO2. Li et al. [19] synthesized a series of trimethylamine hydrochloride·ferric chloride ionic liquids (Et3NHCl·FeCl3 ILs).
The sulfur capacity of 1.5 Et₃NHCl·FeCl₃ ILs at 303.15 K and 101.3 kPa is the highest (2.178 wt%). The oxidation efficiency of H₂S is 1.5 Et₃NHCl·FeCl₃ ILs was up to 87.9%. The solubility of carbon dioxide and hydrogen sulfide gases in the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([C₂mim][OTf]) was measured at temperatures from (303.15-353.15) K and pressures up to about 3.0 Mpa [23]. Researcher have found that pure ionic liquids can effectively absorb H₂S in large quantities, but the practical use of pure ionic liquids in gas separation is limited by their high viscosity and the small gas-liquid interface which limits gas diffusion rates through the ionic liquids [24, 25]. The loading of the ionic liquids on supports can reduce such drawbacks since the ionic liquid can be impregnated on the surface of the support and be retained in liquid state even at high temperatures. Zhang et al. [26] has reported loading 1,1,3,3-tetramethylguanidinium lactate (TMGL) on porous silica particles resulting in high SO₂ sorption rates and capacity compared to pure unsupported TMGL. And Severa et al. [27] found that the 1-ethyl-3-methylimidazolium acetate loaded activated carbon exhibited higher SO₂ sorption capacity than pure activated carbon and 10 % potassium hydroxide loaded activated carbon. However, there has been little research towards the loading of ionic liquids onto activated carbon materials for H₂S removal. The objective of this study is to investigate the process of H₂S adsorption onto activated carbon supported ionic liquids. The performance of impregnation by three different ILs for H₂S adsorption is measured in a fixed bed. The effects of activated carbon substrate, ionic liquid, initial H₂S concentration and the flow rate on the adsorption process are also studied in this work.

2. Experimental

2.1. Materials

Two kinds of activated carbons named AC-1, and AC-2 were obtained from Qingdao Guanbaolin Activated Carbon Co., Ltd., China. 1-ethyl-3-methylimidazolium acetate ([C₂mim][Ac]), 1-ethyl-3-methylimidazolium hydrogen sulfate ([C₂mim][HSO₄]) and 1-allyl-3-methylimidazolium chloride ([C₃mim][Cl]) were purchased from Sigma-Aldrich. Methanol was obtained from Sinopharm Chemical Reagent Co., Ltd., China. N₂/H₂S mixture gas with 75-750 mg·m⁻³ were purchased from Sichuan Zhongce Gas Co., Ltd., China. All above chemicals were used as received. Deionized water was obtained from Barnstead E-pure water purification system in our laboratory.

2.2. Preparation of ionic liquid loaded activated carbon materials

The ionic liquid supported by activated carbons were prepared by the incipient impregnation method at 60 °C. To prepare the materials, about 20.0 g of pure ionic liquid were mixed with 20.0 g methanol (50% (w/w) solution of ionic liquid in methanol) in a 250 ml beaker followed by addition of 50.0 g of activated carbon. The activated carbon and ionic liquid-methanol mixture were allowed to stand for 8 h at 60°C, with occasional agitation. The impregnated activated carbon materials were then dried at 120 °C for up to 12 h in a vacuum oven. The dried ionic liquid loaded activated carbons were stored under nitrogen in a desiccator.

2.3. Characterizations

The nitrogen adsorption/desorption isotherms of activated carbons were determined using an adsorption analyzer ASAP 2020 (Micromeritics Instrument Co., USA) operated at 77 K. The specific surface area was determined using the N₂ isotherms data by means of the Brunauer-Emmett-Teller (BET) method. The total pore volume (Vₑₒₚₑₜ) was estimated to be the liquid volume of nitrogen at a relative pressure of about 0.98. The micropore volume (Vₘᵢｃᵦₒ) was calculated from the N₂ isotherms data by Barrett-Joyner-Halenda (BJH) method. The pore size distributions were calculated by applying the density functional theory (DFT) to N₂ isotherm data.
2.4. **H$_2$S breakthrough measurements**

The H$_2$S breakthrough curves were measured at 25 °C under dry condition. In a typical experiment, 0.2500 g of the sample with the particle size between 450 μm and 600 μm was packed into a adsorption column (internal diameter 10 mm). After the H$_2$S stream passed through the adsorbent bed, the concentration of H$_2$S in the outlet gas was measured using electrochemical sensors (multi-RAE Plus detector from RAE system). Breakthrough experiments were plotted as C vs sorption time (t) wherein C was the measured H$_2$S concentrations at the outlet of the reactor test bed. The breakthrough time for the sorption curves was defined as the time it took the outlet H$_2$S concentration to reach 15 mg·m$^{-3}$ and the breakthrough capacity was the amount of H$_2$S adsorbed by the material during the breakthrough period (from t = 0 up to the breakthrough time). The saturation adsorption capacity of the materials was calculated from time, t = 0 to the time when the outlet concentration reaches to 80% of the inlet H$_2$S concentration.

2.5. **Evaluation of H$_2$S adsorption capacity**

The adsorption capacity $q_m$ was calculated by integrating the area above the breakthrough curve for a given inlet H$_2$S concentration, mass of adsorbents and flow rate, as it is defined by equation (1):

$$ q_m = \frac{Q}{1000m_s} \int_0^t (1 - \frac{C_t}{C_0})dt $$

where $C_0$ is the initial H$_2$S concentration (mg·m$^{-3}$); $C_t$ is the measured H$_2$S concentration at the outlet of the reactor (mg·m$^{-3}$); the $q_m$ is the adsorption capacity (mg/g); $Q$ is the adsorption time (L·min$^{-1}$); $m_s$ is the adsorbent mass (g).

3. **Results and discussion**

3.1. **Characteristics of pure activated carbon supports**

Two commercial activated carbons were used as the effective supports of the ionic liquids during sorption studies. In order to understand more clearly the pore structure of adsorbents, the N$_2$ adsorption-desorption isotherms and pore size distributions of two kinds of activated carbons were shown in Figure 1; the textural properties were included in Table 1.

Both activated carbons had a high BET specific area and total pore volume. The pore size distributions indicated a multi-peak dispersal with a majority of pores having diameters of less than 4 nm. Micropores (defined as pore diameter < 2 nm) formed a majority of the pore volume. As known from Table 1, the surface areas and micropore volumes of AC-1 is significantly greater than the values for AC-2. The micropore volume can be ranked in order of AC-1 and AC-2. This high concentration of micropores was presumed to lead to the entrapment of the ionic liquid deep inside the internal pore structure of the activated carbon, hence mitigating ionic liquid loss from the support.

| Adsorbent | BET (m$^2$·g$^{-1}$) | Average pore diameter (nm) | $V_{total}$ (cm$^3$·g$^{-1}$) | $V_{micro}$ (cm$^3$·g$^{-1}$) |
|-----------|----------------------|---------------------------|-----------------------------|-------------------------------|
| AC-1      | 1031.2834            | 2.2506                    | 0.662987                    | 0.396881                      |
| AC-2      | 849.1151             | 2.2930                    | 0.584033                    | 0.167355                      |
Figure 1. The N\textsubscript{2} adsorption-desorption isotherms at 77 K and pore size distributions of two kinds of activated carbons.

3.2. H\textsubscript{2}S adsorption of pure activated carbon supports

It can be seen from Table 1 that AC-1 porosity may be more suitable than that of AC-2 for IL impregnation and H\textsubscript{2}S adsorption, but in order to choose the better activated carbon support, H\textsubscript{2}S adsorption of both pure activated carbons (AC-1 and AC-2) was tested. Figure 2 shows that the breakthrough curves of 150 mg·m\textsuperscript{-3} H\textsubscript{2}S on two activated carbon samples, where C is the outlet concentration (mg m\textsuperscript{-3}) and t is the adsorption time (min) under the flow rate is 0.1 L·min\textsuperscript{-1}.

As illustrated in Table 2, the breakthrough time and saturation time of AC-1 is longer than AC-2 under the given concentration, meaning that AC-1 has higher breakthrough capacity and saturation capacity. The pore structure parameters of the two activated carbon samples suggest that there is a close relationship between the mass transfer rate internally in the activated carbon and the activated carbon pore structures. The more complex the activated carbon pore structure, the slower the mass transfer rate. From Table 1, it can be seen that the surface areas and micropore volumes of AC-1 is significantly greater than the values for AC-2, thereafter AC-1 can be considered as the better support for ionic liquid.
3.3. H$_2$S removal of ionic liquids loaded activated carbon

To reveal the promotion of impregnation with ionic liquid for H$_2$S adsorption on activated carbon AC-1, dynamic adsorption tests were performed under experimental conditions of 150 mg·m$^{-3}$ H$_2$S in N$_2$, temperature of 25$^\circ$C and flow rate of 0.1 L·min$^{-1}$. As a matter of convenience, three ionic liquid loaded activated carbons were respectively named [C$_2$min][Ac]-AC, [C$_2$min][HSO$_4$]-AC and [C$_3$min][Cl]-AC after AC-1 were loaded with three different ionic liquids. And Table 3 shows the textural properties of three ionic liquid loaded activated carbons. The H$_2$S breakthrough times and breakthrough capacities of ionic liquid sorbents were also shown in Table 4.

**Table 3.** Textural properties of three ionic liquid loaded activated carbons.

| Adsorbent   | BET (m$^2$·g$^{-1}$) | Average pore diameter (nm) | $V_{\text{total}}$ (cm$^3$·g$^{-1}$) | $V_{\text{micro}}$ (cm$^3$·g$^{-1}$) |
|-------------|-----------------------|----------------------------|------------------------------------|----------------------------------|
| [C$_2$min][Ac]-AC | 905.8975             | 2.3215                     | 0.5984                             | 0.3864                           |
| [C$_2$min][HSO$_4$]-AC | 880.2314             | 2.5986                     | 0.5215                             | 0.3281                           |
| [C$_3$min][Cl]-AC | 892.5618             | 2.5267                     | 0.6024                             | 0.3759                           |

**Table 4.** The H$_2$S breakthrough times and capacities of ionic liquid sorbents.

| Adsorbent   | Breakthrough time (min) | Breakthrough capacity (mg H$_2$S/g sample) |
|-------------|-------------------------|-------------------------------------------|
| [C$_2$min][Ac]-AC | 11.12                 | 0.651                                     |
| [C$_2$min][HSO$_4$]-AC | 5.17                   | 0.302                                     |
| [C$_3$min][Cl]-AC | 9.00                   | 0.527                                     |

It can be seen from Table 3 and Table 4, the H$_2$S breakthrough time decreased in the order [C$_2$min][Ac]-AC > [C$_3$min][Cl]-AC > [C$_2$min][HSO$_4$]-AC. The [C$_2$min][Ac]-AC sorbent had the highest breakthrough time of 11.12 min while the rest of the studied ionic liquid loaded activated carbon...
carbons had breakthrough times below 10 min. The pure activated carbon AC-1 had an H$_2$S breakthrough time of 3.63 min indicating that the ionic liquids studied can improve the H$_2$S sorption property compared to pure activated carbon. Meanwhile, the equilibrium sorption capacity of H$_2$S increased more than two times after impregnation, though the BET surface area, micropore volume of the activated carbon was reduced slightly. The impregnation might occupy a portion of the carbon pore volume and surface area, thus limiting physical sorption. Nevertheless, the sorption capacity on the impregnated carbons is much greater than that of the unmodified carbon. The results confirm that after impregnation, H$_2$S is no longer removed mainly by physical adsorption but chemical reaction. The impregnated ionic liquid changes the surface properties and enforced the interactions between activated carbons and H$_2$S molecules.

The above results clearly indicate the importance of testing ionic liquid based materials to screen out ionic liquid based sorbents with potential for H$_2$S removal. The advantage of such supported ionic liquid sorbents is their ability to be utilized attributed to increased gas diffusion through the ionic liquid thin films compared to sorption in pure ionic liquids. Sorption in pure ionic liquids are inhibited by the high ionic liquid viscosity which reduce gas flow through the bulk of the ionic liquid [26].

### 3.4. Effect of H$_2$S concentration on H$_2$S removal

To study the effect of the initial H$_2$S concentration on the adsorption, the breakthrough curves for H$_2$S adsorption on [C$_2$mim][Ac]-AC under temperature of 25°C and flow rate of 0.1 L·min$^{-1}$ were performed. The according breakthrough times and breakthrough capacities were shown in Table 5. The H$_2$S breakthrough time decreased with increasing H$_2$S concentration, but the sorption capacity increased when the inlet H$_2$S concentration increased. For lower feed concentrations, the lower mass-transfer flux was achieved from the bulk gas to the particle surface, due to the decreased driving force. On the other hand, higher feed concentration yields enhanced driving force along the pores, thus resulting in the steeper breakthrough curves and the faster breakthrough.

**Table 5.** The H$_2$S breakthrough times and breakthrough capacity of ionic liquid sorbent at different concentrations

| Concentration [mg·m$^{-3}$] | Breakthrough time [min] | Breakthrough capacity [mg H$_2$S/g sample] |
|-----------------------------|-------------------------|-------------------------------------------|
| 75                          | 26.63                   | 0.522                                     |
| 120                         | 12.00                   | 0.598                                     |
| 150                         | 11.12                   | 0.651                                     |
| 750                         | 2.67                    | 0.802                                     |

### 3.5. Effect of gas flow rate on H$_2$S removal

The effect of flow rate on H$_2$S sorption was performed by analysis of breakthrough curves at flow rates of 0.05, 0.1 and 0.15 L·min$^{-1}$, whilst maintaining other experimental conditions constant (150 mg·m$^{-3}$ and 25°C). The breakthrough times and breakthrough capacities were determined from the breakthrough curves at three flow rates and shown in Table 6. As seen from Table 6, the breakthrough time and breakthrough capacity sorption capacity of the [C$_2$mim][Ac]-AC sorbent decreased with increase in flow rate. At low flow rates of 0.05 L·min$^{-1}$ the H$_2$S residence time on the sorbent is longer (40.13 min) than the high flow rate of 0.15 L·min$^{-1}$ (2.67 min) resulting in effective interaction of H$_2$S molecules with the ionic liquid sorbent as well as increased diffusion of H$_2$S molecules into the ionic liquid sorbent.

**Table 6.** Effect of flow rate on H$_2$S breakthrough times and breakthrough capacities.

| Flow rate (L·min$^{-1}$) | Breakthrough time (min) | Breakthrough capacity (mg H$_2$S/g sample) |
|--------------------------|-------------------------|-------------------------------------------|
| 0.05                     | 40.13                   | 2.327                                     |
| 0.10                     | 11.12                   | 0.651                                     |
| 0.15                     | 2.67                    | 0.154                                     |
4. Conclusions

In this work, experiments on H₂S adsorption performance of ionic liquid loaded activated carbon at different conditions are presented. The results show that the ionic liquids studied can improve the H₂S sorption property compared to pure activated carbon. Under the experimental conditions the [C₂mim][Ac] loaded activated carbon exhibited superior performance compared with other ionic liquids. The [C₂mim][Ac] sorbent breakthrough time (11.12 min) was greater than pure activated carbon (3.63 min) indicating the high potential of the ionic liquid sorbent for removing H₂S. The effect of inlet H₂S concentration on the dynamic adsorption process was significant. The H₂S breakthrough time decreased with increasing H₂S concentration, but the sorption capacity increased when the inlet H₂S concentration increased. In addition, the gas flow rate significantly impacted the H₂S breakthrough times of [C₂mim][Ac] sorbent, low flow rates resulted in the longest breakthrough time. These findings in this work indicate that ionic liquid loaded materials may result in the development of practical ionic liquid sorbents with potential for use in flue gas desulfurization and H₂S filtration of polluted air. In addition, the effect of humidity on H₂S removal efficiency and the regeneration performance of activated carbon supported ionic liquids will be investigated in the future.

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