Removal of hydrogen sulfide using palygorskite in a fixed bed adsorber

T. Higuchi, Q. Zhang, M. Sekine, T. Imai and K. Yamamoto

ABSTRACT

This work describes the use of a novel palygorskite, a type of magnesium aluminium silicate clay possessing a high specific surface area and pore surface activity, as a low cost and highly efficient adsorbent for hydrogen sulfide (H2S) removal. Adsorption of H2S on palygorskite pretreated with acid or base was investigated in a fixed bed adsorber. The samples after base pretreatment had better dynamic adsorption performances than raw material and samples pretreated with acid. The H2S adsorption capacity decreased with an increase in inlet H2S concentration. This can be interpreted by the fact that H2S adsorption on the surface of palygorskite is chemisorption. The adsorption capacity increased from 25 to 50 °C, then decreased from 50 to 100 °C, which indicates that chemisorption took place and its better reaction temperature was around 50 °C.

Key words | adsorption capacity, fixed bed adsorber, hydrogen sulfide, palygorskite

INTRODUCTION

Much effort has been devoted to the elimination or reduction of odour emissions from various sources. Many techniques including catalytic decomposition, reaction with another gas, adsorption with solids and combustion can be applicable to reduce or eliminate odour emissions. Among these techniques, adsorption of odour onto adsorbents is one of the more promising methods and a fixed bed adsorber is generally used. The key factor of this process is mainly dependent on an appropriate adsorbent which possesses the ideal properties for the selective adsorption of odour. The commonly used commercial adsorbents, such as activated carbon, zeolites and silica gel, were extensively studied for their odour adsorptive properties. Most of these adsorbents, however, have disadvantages such as complicated treatment processes or energy consumption, which increase the odour removal costs. For further minimization of process costs for odour removal, investigations have focused on using cheaper and easily obtainable adsorbents.

Recent studies (Zhang et al. 2008, 2009; Higuchi et al. 2010) revealed that palygorskite was a low cost and highly efficacious adsorbent for elimination of ammonia (NH3) and sulfur dioxide (SO2). Palygorskite, formed in an arid environment, is a species of magnesium aluminium silicate clay with a unit cell formula of Mg5−y−zR3+[x−x]Si8−xR3+/2(x+y−2z)(OH)2(OH2)y(OH)2/E2+[x−y−2z]/2(H2O)4. Normally, R3+ is Al3+ and Fe3+; □ stands for the octahedral voids; E2+ stands for the exchangeable cation (Bradley 1940; Corma et al. 1990; Huang et al. 2007). It has a 2:1 layered structure with talc-like T-O-T ribbons that expand along the axis of the fibres. Due to its unique structure and considerably textured property, palygorskite has received considerable attention and been used in a number of different applications such as industrial, catalytic and environmental use (Hassen et al. 2003; Chen et al. 2007; Chen & Wang 2007; Wang et al. 2007).

The previous papers (Zhang et al. 2008, 2009; Higuchi et al. 2010) showed that palygorskite pretreated with hydrochloric acid (HCl), nitric acid (HNO3) or sodium hydroxide (NaOH) considerably changed the adsorption properties for NH3 and SO2 removal. The acid (HCl and HNO3) activation is an efficient method to improve the surface properties because it can modify the number of adsorption sites by disaggregation of palygorskite particles, eliminate mineral impurities and increase its surface area. Pre-treatment with base (NaOH) can get silica gel that has a good ability to adsorb gases.

In this study, the adsorption capacity of raw palygorskite and palygorskite pretreated with HCl, HNO3 or NaOH for H2S removal following the change of H2S concentration and the temperature is investigated.

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MATERIALS AND METHODS

Preparation of adsorbents

Palygorskite clay was supplied by Gansu KaiDi Ecosystem Agriculture Co., Ltd, Gansu province, China and milled into a size of 400-mesh (around 38 μm). Palygorskite samples were prepared by the following procedure: micro-powdered palygorskite was immersed in a solution of HCl, HNO₃ or NaOH at various concentrations (1, 3 or 6 mol L⁻¹) at 20 or 50 °C for a given time (24 or 48 h) with mechanical mixing at 150 rpm. The powder was then washed with distilled water several times until the pH was neutral, granulated into small particles with sieves and dried at 105 °C for 24 h prior to adsorption experiments. The pre-treatment conditions and the specific surface area (SSA) of the samples are shown in Table 1. The SSA of the samples were measured by a Quantachrome AUTOSORB-1 (Giangarlo Scientific Co., Inc., USA) at 77 K using nitrogen as adsorbate and calculated from the isotherm using the Brunauer-Emmett-Teller (BET) equation. The name of each sample represents the pre-treatment conditions. For example, NaOH-154 indicates pre-treatment of palygorskite with 1 mol L⁻¹ NaOH solution at 50 °C for 48 h.

Adsorption experiments

Adsorption experiments were carried out by a dynamic method on a laboratory scale as shown in Figure 1. The experimental conditions are summarized in Table 2. After the pure nitrogen gas flowed through the system for 5 min, a plastic bag was charged with the designated initial concentration of H₂S with nitrogen as balance and the precisely weighed adsorbent contained in a column was connected. The input flux of H₂S was adjusted and measured by the flow meter. Then the inlet and outlet concentrations (Cᵢ and Cₒ, respectively) were tested at the sampling ports A and B in Figure 1 using a gas detection tube (Gastec Corp., Japan). The adsorbent in the column was installed in a thermostatic oven (G2800, Yanaco Co., Ltd., Japan) to keep the temperature constant. Adsorption experiments were conducted once for each condition until Cₒ increased to over 10% of Cᵢ.

Table 1 | Pretreatment conditions and specific surface area (SSA) of samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reagent</th>
<th>Concentration (mol L⁻¹)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>SSA (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RM (Raw material)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>108</td>
</tr>
<tr>
<td>HCl-322</td>
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<td>3</td>
<td>20</td>
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<td>154</td>
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<td>50</td>
<td>24</td>
<td>213</td>
</tr>
<tr>
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<td>1</td>
<td>20</td>
<td>24</td>
<td>109</td>
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<td>50</td>
<td>48</td>
<td>102</td>
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<tr>
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<td>50</td>
<td>48</td>
<td>99</td>
</tr>
<tr>
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<td>6</td>
<td>50</td>
<td>48</td>
<td>84</td>
</tr>
</tbody>
</table>

Figure 1 | Schematic diagram of experimental setup.
RESULTS AND DISCUSSION

Effect of pretreatment

The breakthrough curves for H$_2$S adsorption by RM and different pretreated samples, carried out with an inlet concentration of 40 ppm, are shown in Figure 2. The operating variables (adsorbent weight, particle size and gas flow rate) were kept identical in each case and the runs were carried out at the laboratory room temperature of 25°C. The 10% breakthrough time (10%BT: the time taken for $C_o$ to reach 10% of $C_i$) and adsorption capacity ($W$) at 10%BT in the adsorption experiments at 25°C are summarized in Table 3. The samples after base pre-treatment had better dynamic adsorption performances, evident by longer 10%BT and larger corresponding adsorption capacities than RM and samples pretreated with acid. NaOH-154 had the highest H$_2$S adsorption capacity at inlet concentration of 40 ppm. As OH$^-$ is present in the samples of NaOH-154 and NaOH-354, the results suggest that the important factors for adsorption of H$_2$S also include chemical interaction with hydroxyl species and their dispersion and location on the surface of the clay. With an increase in NaOH concentration, the 10%BT and adsorption capacity decreased, implying that the higher NaOH concentration destroyed the structure of palygorskite (Zhang et al. 2009).

Effect of H$_2$S concentration

The experiments with NaOH-154 and NaOH-354 were carried out at 25°C under varying gas inlet concentrations: 40, 80 and 130 ppm. The operating variables including adsorbent weight and gas flow rate were kept identical in each case. The 10%BT and adsorption capacity at 10%BT with different inlet concentration of H$_2$S are summarized in Table 3. As shown in Figure 3, the H$_2$S adsorption capacity decreased with an increase in inlet H$_2$S concentration in the gas. The adsorption capacity of NaOH-154 decreased from 3.1 to 2.8 mg g$^{-1}$ with an increase in inlet H$_2$S concentration from 40 to 130 ppm. The sample of NaOH-354 showed similar phenomena to the NaOH-154 and the adsorption capacity decreased from 1.0 to 0.30 mg g$^{-1}$. This can be interpreted by the fact that H$_2$S adsorption on the surface of palygorskite is chemisorption. For the chemisorption, the surface can only form monolayer adsorption

![Figure 2](image-url)
and it also needs time to reach equilibrium. In the given contact time, limited molecules of H₂S were adsorbed and the 10%BT became shorter with an increase in inlet H₂S concentration, which resulted in the decrease of adsorption capacity.

Effect of temperature

Adsorption experiments were carried out at various adsorption temperatures using NaOH-154. The results are shown in Figure 4. It describes the adsorption capacity of H₂S at 10%BT during dynamic adsorption by palygorskite at temperatures of 25, 40, 50, 75 and 100 °C. The gas flow rate and inlet concentration of H₂S were kept constant at 0.1 L min⁻¹ and 80 ppm, respectively. It was observed that the adsorption capacity of NaOH-154 increased from 25 to 50 °C, then decreased from 50 to 100 °C. The adsorption capacity at 50 °C showed the maximum of 5.7 mg g⁻¹ although it was lower than that of previous studies using activated carbons (Guo et al. 2007; Ros et al. 2007). These results indicate that chemisorption took place and its better reaction temperature was around 50 °C.

CONCLUSIONS

Adsorption of H₂S on palygorskite pretreated with acid or base was investigated in a fixed bed adsorber. The samples after base pre-treatment had better dynamic adsorption performances than raw material and samples pretreated with acid. The H₂S adsorption capacity decreased with an increase in inlet H₂S concentration. This can be interpreted by the fact that H₂S adsorption on the surface of palygorskite is chemisorption. The adsorption capacity increased from 25 to 50 °C, then decreased from 50 to 100 °C, which indicates that chemisorption took place and its better reaction temperature was around 50 °C.

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REFERENCES


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