A NOVEL AND COST-EFFECTIVE REMOVAL OF SILOXANES FROM WASTEWATER DIGESTER BIOGAS USING REGENERABLE POLYMERIC ADSORBENTS

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Abstract—biogas, a fuel used to generate electricity, contains siloxanes that can damage combustion engines, leading to expensive repairs and service interruptions. Thermal swing adsorption (regeneration at 250 °C) using silica gel is an effective method to remove siloxane from biogas. In the present study, a novel polyacrylic acid (paa)-based polymer adsorbent was studied as a biogas siloxane adsorbent exposed to adsorption/regeneration cycles. The exhausted polymer adsorbent was regenerated by washing with heated air at 60–80 °C, which afforded a similar capacity for siloxane (D5) adsorption. At room temperature (25 °C), the siloxane adsorption capacity of this polymer was ~80% of that of silica gel. In addition, the thermal desorption of siloxane (D5) from the polymer was more than 95% at a low regeneration temperature of 80 °C, where no siloxane regeneration was observed using conventional silica gel.

Index Terms—Biogas, Siloxane, Adsorbent, Polymer

I. INTRODUCTION

Volatile organic silicon compounds, including siloxanes, are one of the biggest challenges in the utilization of biogas to generate energy. In a majority of most wastewater treatment plants (WWTPs), sludge is stabilized by anaerobic digestion.[1] This digestive process produces biogas, which is comprised of various gases such as like methane (60–70%), CO2 (30–40%), nitrogen (<1%), H2S (10–2,000 ppm), and siloxane (30–60 ppm).[2] Biogas is arguably a more versatile renewable energy source as compared to wind and solar energy because of its determinate energy value and ease of storage. Therefore, the potential utilization of biogas is significantly independent of such factors such as geographical location and season.[3] Biogas can be used directly for heating and the generation of electricity, as well as a substitute for fossil fuel applications, e.g., as transport fuel.[4] Currently, internal combustion engines and gas combustion turbines are the best developed technologies for biogas-to-electricity projects. However, when biogas is used as a fuel for the generation of electricity, the siloxanes contained in the biogas can damage combustion engines, leading to expensive repairs and an interruption of service. The most adverse effect of the utilization of biogas obtained from the anaerobic digestion of wastewater sludge stems from volatile methylsiloxanes (VMS). During combustion, siloxanes are converted into silicon dioxide deposits, which lead to the abrasion of engine parts or the build-up of layers that inhibit the essential conduction of heat or lubrication.[5]

The common VMS compounds in biogas plants that process sewage sludge are octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5).[6] In some instances, activated charcoal is used to reduce the silicon content. Yet, because siloxanes are difficult to desorb from the material, the adsorbent beds have to be replaced regularly. However, it has been indicated that silica gel (SG) exhibits a superior adsorption capacity for siloxanes (more than 100 mg/g). Additionally, it was observed that SG has an excellent desorption efficiency of more than 95% for both the L2 and D5 siloxanes at 250 °C for 20 min. However, it would be advantageous and cost-effective, if the adsorption material could be regenerated easily at a lower temperature.[7]

Figure 1 SEM images of regenerable (a) polymeric adsorbent (RPA) and (b) silica gel (SG) used in this study

In the present study, we investigated a novel regenerable polymer adsorbent (RPA), based on polyacrylic acid (PAA), for its ability to remove siloxane from biogas and its performance in subsequent low-temperature regeneration. This PAA-based polymer was introduced as desiccant for water vapor adsorption and low-temperature regeneration in our previous study.[8] This material, called a super desiccant polymer (SDP), was...
developed by the ion modification of polyacrylic acid (PAA) sodium salt, which exhibits an excellent water vapor sorption capacity, much higher than that of silica gel. Fig. 1 shows the SEM images of both the polyacrylic acid polymer and the silica gel used in the present study.

II. EXPERIMENTAL

A. Materials and methods

To evaluate the adsorption capacity of the reusable polymeric adsorbent (RPA) and the silica gel (SG), fixed-bed experiments were performed at room temperature (25 °C) and at dynamic conditions in the adsorption-desorption apparatus (Fig. 2), by allowing a flow of feedstock with a known inlet concentration of D5 through the bed, and then monitoring the outlet concentration, the adsorption capacity was measured. The breakthrough experiments were considered complete when the outlet concentration of D5 had reached the pre-set level of 10% of the inlet concentration (~4,300 mg/Nm³). The siloxane adsorbed onto the sample (in mg) was calculated as the difference between the siloxane that would have passed through in the absence of an adsorbent (calculated by the plateau value at complete saturation of the carbon sample) and by integrating the breakthrough curve over time until the incipience onset of the 10% breakthrough. The molecular weight of D5 siloxane is 370.77 g·mol⁻¹ and the boiling point is 210 °C (483 K).

To evaluate the possibility of low temperature regeneration of the RPA, the thermal desorption of siloxane was studied using the same apparatus. After the 10% breakthrough of the adsorbent was achieved, the adsorbent bed was placed under a pure nitrogen flow. The column was kept under the flow of pure nitrogen at room temperature for 40 min, while being heated at a constant rate of 1 °C/min to 60 °C. In the SG case, the column was heated again at 10 °C/min to 150 °C, and held for 40 min. During this experiment, a continuous on-line analysis of the downstream gas was performed using gas chromatography and flame ionization detection (GC/FID).

III. RESULTS AND DISCUSSION

B. Adsorption of siloxanes (D5) by the polymer adsorbent (RPA)

Figure 3 shows the typical outlet concentrations of D5 siloxane from the adsorbent bed versus time for the reusable polymer adsorbent. The D5 siloxane concentration in the gas was measured by GC/FID at the fixed inlet D5 concentration (4,000 mg m⁻³) and a flow rate of 200 mL min⁻¹ at 25 °C. The outlet concentration of siloxane remains almost zero and the removal efficiency is nearly 100% up to 400 min. The removal efficiency continuously decreased and reached 40% after 1,000 min.

The breakthrough point of the adsorbent bed is considered to be when the outlet D5 siloxane concentration reaches 10% of the inlet concentration and the removal efficiency of D5 siloxane is 90%. In this figure, the 10% breakthrough time of RPA is 700 min, and the 90% breakthrough time is 1,100 min.

Figure 4 compares removal efficiency of D5 siloxane from the fixed-bed adsorbents versus time for four different adsorbents (silica gel, RPA, zeolite, and active carbon). (Inlet D5 concentration was ~4,000 mg m⁻³ and the flow rate was 200 mL min⁻¹ at 25 °C). On the basis of similar bed densities, the ranking of 10% breakthrough time for the bed types was silica gel (1,128 min), RPA (703 min), zeolite (570 min), and active carbon (462 min). The adsorption capacity of RPA is less than silica gel, but it is better than zeolite and activated carbon.
Table 2 summarizes the adsorption capacities for the D5 siloxane of RPA, and three other common adsorbents (silica-gel, zeolite, and activated carbon) for siloxane removal, which is the cumulative amount of D5 adsorbed, up to a 10% breakthrough point. This was a dynamic adsorption test where the inlet D5 concentration was 4,000 mg m⁻³, adsorbent mass was 35 g, the flow rate was 200 mL/min, and the relative humidity was 75%. The D5 adsorption capacity of RPA was 21.55 mg/g adsorbent, which is ~70% of the adsorption capacity of silica gel. However, it is better than both zeolite and activated carbon. The BET surface area of RPA was 120 m²/g, which is the smallest among the four adsorbents. The D5 adsorption capacity of the adsorbent was not directly proportional to the specific surface area. This means that the D5 adsorption mechanism is not the only factor controlling physical adsorption on the adsorbent surface.

Table 2 Adsorption capacity for D5 siloxanes as a function of adsorbent material

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity for D5 (mg/g)</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica-gel</td>
<td>31.2</td>
<td>470</td>
</tr>
<tr>
<td>RPA</td>
<td>21.55</td>
<td>120</td>
</tr>
<tr>
<td>Zeolite</td>
<td>15.0</td>
<td>1000</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>15.0</td>
<td>1000</td>
</tr>
</tbody>
</table>

C. Effect of relative humidity on adsorption of siloxanes (D5) by the reusable polymer adsorbent (RPA)

Figure 5 shows the D5 adsorption capacity of the RPA and SG with changes in the relative humidity of the carrier gas. In this experiment, the D5 siloxane adsorption capacity of silica gel was 77.39 mg/g at RH = 25%, which is similar to the result of Ref. [10] in a dry condition (~100 mg/g). It drastically decreased to 35.24 mg/g at RH = 100%, mainly due to the competition between water vapor and siloxane on adsorption.

However, RPA was found to be humidity-resistant in both dry (27 mg/g) and fully saturated (25 mg/g) conditions. This phenomenon is mainly due to the difference in adsorption mechanisms between siloxane and water vapor on this substance, but also partly due to the large desiccant capacity of this substance.

D. Regeneration Experiment of RPA

Figure 6 shows the measured D5 concentration at the outlet of the adsorption bed versus time. The regeneration temperature was 60 °C (RPA) and 150 °C (silica gel), instead of high temperature regeneration (250 °C) for silica gel, which improves the cost effectiveness of this process. This figure indicates that an excellent initial desorption of the new RPA was observed for the siloxane D5 at a relatively low temperature (60 °C) with gas circulation. The D5 concentration was greater than 40,000 mg/m³, and regeneration was complete in a short period of time (~40 min). In a similar experiment using SG as the adsorption material, no desorbed siloxane was detected until 100 °C, and the desorption efficiency of D5 was less than 10% by thermal desorption even at 150 °C.

E. Recyclability of RPA in multiple adsorption–desorption cycles for D5

Figure 7 shows the recyclability of RPA in multiple adsorption–desorption cycles. The adsorption
breakthrough curves of regenerated RPA for D5 siloxane are also evident, along with the removal efficiency of D5 by the adsorbent RPA at room temperature (25 °C). The test conditions were 50 mL/min D5 in N2, an inlet D5 concentration of 1,700 mg/m3, and a sample size of 500 mg. The three D5 siloxane adsorption tests showed almost identical results after 2 h of regeneration (desorption) of RPA at 60 °C for each experiment.

CONCLUSION

We investigated the use of a novel regenerable polymer adsorbent for the removal of siloxane from biogas and its subsequent low-temperature regeneration. This material offered a number of advantages for siloxane removal, in particular its recyclability for use in multiple adsorption-desorption cycles. At room temperature (25 °C), the siloxane (D5) adsorption capacity of the RPA was 21 mg D5 per gram of RPA material, which is approximately 70% that of SG. However, the thermal desorption of siloxane (D5) from this polymer material was almost 100% at a low regeneration temperature of 60 °C, whereas no siloxane regeneration was observed with silica gel under the same conditions. Furthermore, siloxane desorption from SG was low at an even higher regeneration temperature (5% at 150 °C). This novel adsorbent material, therefore, offers the advantage of more effectively regenerating adsorption beds at lower temperatures.

REFERENCES