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Low-temperature regeneration of novel polymeric adsorbent on decamethylcyclopentasiloxane (D5) removal for cost-effective purification of biogases from siloxane

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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. Activated charcoal is used to reduce the silicon content. Since siloxanes are difficult to desorb from the material, the adsorbent beds have to be replaced regularly. Thermal swing adsorption (regeneration at 250 °C) using silica gel is an effective method to remove siloxane from biogas. Also, it would be advantageous and cost-effective if the adsorption material could be regenerated easily at a lower temperature. In the present study, a novel polyacrylic acid (PAA)-based polymer adsorbent was studied as a biogas siloxane adsorbent exposed to adsorption/regeneration cycles. At room temperature (25 °C), the D5 adsorption capacity of RPA was 21.55 mg/g adsorbent, which is ~70% of the adsorption capacity of silica gel. The thermal desorption of siloxane (D5) from the exhausted polymer was more than 95%, which afforded a similar capacity for siloxane (D5) adsorption, at a low regeneration temperature of 80 °C, where no siloxane regeneration was observed using conventional silica gel.

1. Introduction

In most wastewater treatment plants (WWTPs), sludge is stabilized by anaerobic digestion [1]. This digestive process produces biogas, which comprises various gases like methane (60–70%), CO_2 (30–40%), nitrogen (<1%), H_2S (10–2000 ppm), and siloxane (30–60 ppm) [2]. Biogas is arguably a more versatile renewable energy source compared to wind and solar energy because of its determinate energy value and ease of storage [3]. Therefore, the potential utilization of biogas is significantly independent of factors such as geographical location and season. Biogas can be used directly for heating and generation of electricity, and 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. Volatile organic silicon compounds, including siloxanes, are one of the biggest challenges in the utilization of biogas to generate energy. 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 most common VMS compounds found 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. Since siloxanes are difficult to desorb from the material, the adsorbent beds have to be replaced regularly. However, it has been found that silica gel (SG) exhibits a superior adsorption capacity for siloxanes (more than 56 mg/g).7 Additionally, it was observed that SG has an excellent desorption efficiency of L2 (95%) and D5 (74–83%) siloxanes at 250 °C for 20 min [7]. However, it would be advantageous and cost-

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effective if the adsorption material could be regenerated easily at a lower temperature.

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 (dehumidification) 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.

2. Experimental

2.1. 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 (~4300 mg/Nm^3). 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 onset of 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 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).

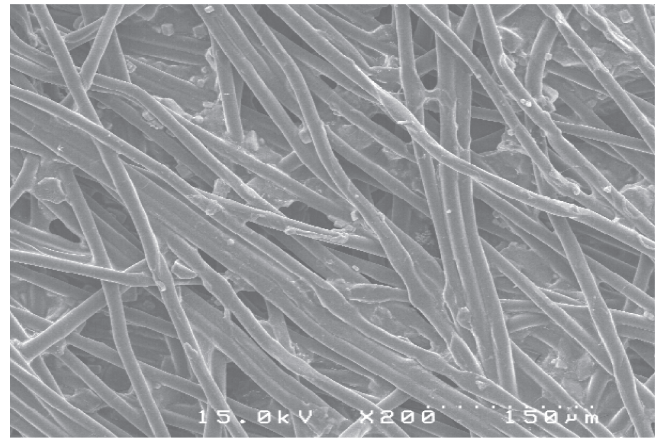
3. Results and discussion

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

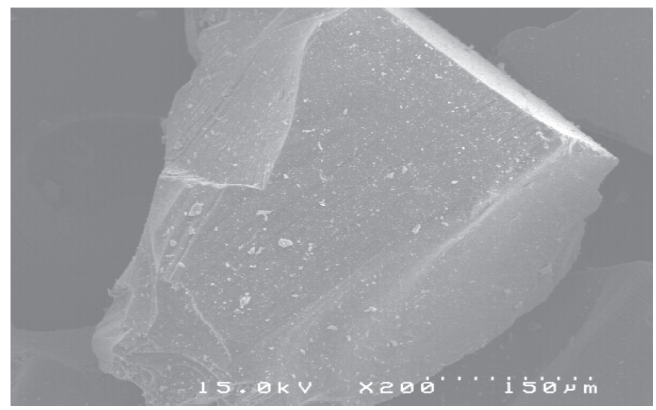
Fig. 3 shows the typical outlet concentrations of D5 siloxane from the adsorbent bed versus time for the reusable polymer adsorbent. The D5 siloxane concentration in the gas was measured by GC/FID at the fixed inlet D5 concentration (4000 mg m^{-3}) and a flow rate of 200 mL min^{-1} at 25 °C. The outlet 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 1000 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 1100 min.

Fig. 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 ~4000 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 (1128 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.



(a) RPA(bulk density : 0.142g/ml)



(b)SG(bulk density : 0.768g/ml)

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

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 4000 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 m^2 /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.

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

Fig. 5 shows the D5 adsorption capacity of the RPA and SG with