ANALYSIS OF MANURE DIGESTATE AND ITS MAJOR COMPONENTS AS ADSORBENTS SOLIDS FOR BIOGAS CLEANING

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Biogas generation through anaerobic co-digestion provides an attractive opportunity to valorize energetically some organic residues generated in intensive livestock farming, as manure. The biogas is mainly composed of CH_4 (50 to 70 vol%), CO_2 (30 to 50 vol%), and trace amounts of other components such as H_2S and could be used as energy source on the farm itself. However, the concentration of CO_2 and H_2S, should be reduced to limit gas emission and broaden biogas fuel applications, because the high concentration of CO_2 in biogas results in a reduced caloric value and the H_2S is corrosive and toxic.

An alternative for cleaning this biogas is to use biochar obtained from the pyrolysis of the solid fraction digestate as low-cost adsorbent. A method that can contribute to sustainable waste management and circular economy in livestock areas is the integration of thermochemical treatments, such as pyrolysis, together with the anaerobic digester, to obtain a low-cost adsorbent. Through pyrolysis of the solid digestate of manure (SDM), the biomass is thermally decomposed in an inert atmosphere to obtain a solid (char) with suitable structural and textural properties for its use in capturing CO_2 and H_2S. The composition of SDM is highly variable depending on the type of farm, the residues co-digested with manure, animals feeding and even the season of the year in which it is collected. Therefore, it is necessary to analyze the effect of SDM composition on the preparation of the char and its capability to retain H_2S and CO_2. This analysis can be approached through the analysis of the adsorption behavior of the carbonaceous solids obtained from the main organic components of SDM, such as cellulose, lignin and proteins. In the current study, the CO_2 an H_2S adsorption behaviors of chars prepared by pyrolysis of SDM, cellulose, lignin and soybean protein, have been investigated at room temperature.

Pyrolysis experiments of SDM and of its main organic components (cellulose, lignin and protein) have been carried out in a fixed-bed reactor of 5 – 10 g capacity at 750 °C with a heating rate of 10 °C/min and maintaining for 1 h the final temperature under 45 mL(STP)/min of N_2. The CO_2 and H_2S adsorption capacities, individual and competitive adsorption, of the produced pyrolysis chars have been studied in a fixed-bed reactor equipped with a mass spectrometer to monitor the effluent gas composition. In each experiment, 0.6 g of char was packed in the fixed-bed. The concentrations of CO_2 and H_2S in the gas were set at 40 vol% and 0.7 vol%, respectively, with a total flow rate of 65 mL(STP)/min of gas. The adsorption tests involved both an adsorption at 25 °C and desorption at 150 °C cycle of CO_2 and H_2S. The adsorption capacity of the chars with both gases has been calculated from the adsorption – desorption curves. The content of sulfur remaining in the chars after the H_2S adsorption – desorption cycle was analyzed (elemental analyzer LECO CHN628 with sulfur analyzer module) to quantify the sulfur chemically retained in the char.

The specific surface area of the chars has been determined by adsorption tests with N_2 at 77 K and CO_2 at 273 K. Data from N_2 adsorption isotherms have been analyzed according to Brunauer-Emmett-Teller (BET) model, while data from CO_2 isotherms have been analyzed with Dubinin-Radushkevich (DR) theory and non-local density functional theory (NLDFT), by assuming slit pore geometry, to determine the pore size distribution.

Cellulose and lignin chars present higher CO_2 and H_2S adsorption, BET surfaces and micropore volumes than char from soybean protein and SDM. In the case of these first materials, the analysis of their structural properties showed a direct relationship between the adsorption capacity and both the surface area and the micropore volume. The lignin and SDM chars showed a greater chemical retention of sulfur while the cellulose char does not present chemisorption. In the case of competitive adsorption, the presence of H_2S in the gas decreases the CO_2 adsorption capacity in the chars.