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Adding Value to Sugarcane Bagasse Ash: Potential Integration of Biogas Scrubbing with Vinasse Anaerobic Digestion

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Abstract: One of the byproducts of sugarcane bagasse combustion in sugarcane mills is sugarcane bagasse ash (SCBA), which contains up to ~40 mass% of organic matter. Currently, SCBA is partially used as a soil fertilizer. However, SCBA's poor content of minerals, which are required by soils, restricts its use in soils, resulting in the disposal of large amounts of SCBA in landfills. Alternatively, SCBA has shown promise for some environmental applications such as wastewater treatment, but its use in gas cleaning deserves further study. The objective of this work was to assess the use of as-received SCBA to remove hydrogen sulfide (H_2S) from biogas, thus, to add value to the ash. The experimental procedure consisted of passing biogas containing H_2S through a column with SCBA and monitoring the H_2S content inline by employing a gas chromatograph until the concentration of H_2S, measured after the column, was ~10% of the original concentration. The breakthrough time of the SCBA adsorption curve was ~75% the breakthrough time observed with activated carbon, showing that SCBA could be a cheap alternative to commercial materials that are currently used for biogas scrubbing. This result could positively impact ethanol sugarcane mills that need to clean biogas produced from vinasses, as part of a strategy to integrate biogas production and cleaning operations using low-value residues (i.e., vinasses and ash). SCBA's capacity for removing H_2S from biogas results from the presence of K-compounds (e.g., K_2SiO_3 and $K_2Si_2O_5$) on the ash's surface and its relatively high porosity. Additionally, S-enriched SCBA (due to H_2S retention) can expectedly be more beneficial to soils than directly adding the ash since S is an essential nutrient for the growth of plants.

Keywords: sugarcane bagasse; ash; biogas scrubbing; hydrogen sulfide

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1. Introduction

Sugarcane is the most cultivated crop worldwide. According to the Food and Agriculture Organization of the United Nations [1], the total area cultivated with sugarcane globally in 2021 was approximately 26.35 million ha, resulting in the production of ~1.86 billion tons of sugarcane. An important byproduct of the sugarcane industry is sugarcane bagasse, which is used as a fuel to generate steam for cogeneration (i.e., the combined production of sugar and/or ethanol and electricity). One of the residues from sugarcane bagasse combustion is sugarcane bagasse ash (SCBA). SCBA normally refers to fly ash, which is released through the boiler's chimneys, but the term can include the boiler's bottom ash. Fly ash is removed from the exhaust combustion gases by using electrostatic precipitators and filters (i.e., dry routes) or gas washers (i.e., wet routes). The wet route is the method that is normally adopted for this in the sugarcane industry. As such, a water scrubbing process is employed to remove the ash. This process consists of a water flocculation step, followed by sedimentation and vacuum filtering, which produces ash with a moisture content of approximately 50% [2–4]. The bottom ash is sometimes mixed with the wet fly ash. However, the material of interest in most works related to SCBA is fly ash, although this is not always explicitly stated in the literature.

SCBA (i.e., fly SCBA) contains up to 35–40 mass% organic matter (i.e., charcoal) and the rest corresponds to inorganic materials (mostly silica). One ton of sugarcane contains up to 25 kg of ash [2,5,6]. Hence, large amounts of SCBA are available in sugarcane-producing countries [7]. One method for partially using SCBA is as a soil fertilizer. However, it has been reported that this material is poor in some minerals that are needed for efficient soil fertilization purposes, which limits its use as a fertilizer [2,8]. Moreover, the particle size distribution of SCBA shows that most of its particles have sizes below 100 μm [9]. The presence of small silica particles and char fines makes the recovery and use of this material challenging [10,11]. Therefore, SCBA is often disposed of in landfills as waste [12–16] and occupies large landfill spaces [17,18], resulting in both environmental and economic issues [19].

New interest in adding value to SCBA has arisen in recent years. This ash has been suggested for several value-added uses, including environmental applications and construction materials. Several works on the uses of SCBA have appeared in recent years, and a number of reviews (e.g., [15,17,18]) have compiled such works. The cement and construction material industries are the sectors with the highest potential for employing large quantities of SCBA [18,20–25]. However, as identified by Gopinath et al. [6], options for the valorization of byproducts of the sugarcane industry should be considered, together with their conversion into cement and construction materials, to minimize waste.

Prior to some uses of SCBA, the organic part is removed from the inorganic one, for example, via floatation in water [26,27]. The inorganic fraction is constituted by SiO_2 (~43–90%), Al_2O_3 (up to 11%), Fe_2O_3 (up to 8%), CaO (up to 22%), and other compounds [2,9]. This fraction can be used as an additive in the concrete and the ceramic industries [2,14,28–34] as an alkali-activated binder [35], or in the manufacturing of composites [32]. The organic fraction can be used, for example, in wastewater treatment after an activation process [27,36] and as a catalyst support to prepare magnetic SCBA for tetracycline removal from wastewater [37]. Nevertheless, some works employ SCBA as-received (i.e., without removing the inorganic fraction). As-received SCBA has been assessed for removing the following: (a) pesticides (fipronil) [38]; (b) the dye reactive red 198, after mixing it with acid-activated bentonite [39]; and (c) phenols and other types of dyes from wastewater [40,41]. As-received SCBA can also serve in the treatment of cooking oil waste [42] and as an adsorbent for the removal of ammoniacal nitrogen from landfill leachate. A study by Mor et al. showed that this type of ash can remove up to 60% of ammoniacal nitrogen (50 mg/L strength) in landfill leachate at a 20 g/L dosage and 180 min of contact time, with an adsorption capacity of 0.31 mg/g [30]. As-received SCBA has also proven effective for improving the properties of expansive soils during road building [11] and as an additive in stone mastic asphalt [19]. Furthermore, SCBA can serve in the adsorption of toxic compounds during the anaerobic digestion of vinasse in sugarcane mills [43].

Despite the potential of biomass combustion ashes in environmental applications [44], our literature review suggests that the possibility of using SCBA for biogas treatment, specifically for hydrogen sulfide (H_2S) removal, has yet to be reported. H_2S in biogas is an undesirable contaminant that corrodes metallic parts of gas engines [45] or gas turbines [46]. As such, H_2S removal from biogas is a pressing necessity. Current processes and materials for biogas cleaning include the following: (a) the addition of iron salts before the digestion process, (b) oxygen injection to the digester, and (c) biological treatment post-digestion using adsorbents, such as iron sponges or activated carbon [45]. Adsorption is the method that is most commonly used. However, the sorption materials can be expensive, have a limited lifespan, and/or need regeneration. Therefore, the use of alternative cheap and locally available materials that do not require regeneration can positively impact the economic viability of the biogas cleaning process.

The use of as-received SCBA for biogas cleaning could benefit the sugarcane industry. Biogas production in these mills is expected to increase globally due to the necessity of the proper management of vinasses derived from ethanol production [47,48] and the potential of processing vinasses via anaerobic digestion [46,49]. Previous studies have shown that chars from biomass gasification are promising materials for use in H_2S scrubbing from biogas [50,51]. Herein, it is hypothesized that as-produced SCBA can also perform adequately in the removal of H_2S from biogas. Therefore, the objective of this work is to assess the potential of using as-received SCBA for removing H_2S from biogas to make the biogas appropriate for further use in sugarcane mills, as part of an integral use of sugarcane residues. At an industrial scale, biogas cleaning is an essential process for removing impurities. This study represents a first step in exploring the potential of SCBA for the removal of H_2S from biogas, with promising implications for its application in sugarcane mills. The research highlights the innovative use of SCBA in biogas purification, which simultaneously enriches it with sulfur for improved performance as a soil nutrient.

2. Materials and Methods

Approximately 5 kg of randomly selected sugarcane bagasse ash (fly ash), obtained from a boiler operating at flame temperature of approximately 1000 °C, was supplied by the "Ingenio San Carlos" sugarcane mill (Province of Guayas, Ecuador; 2°12′33.9″ S, 79°25′59.9″ W). This mill processes up to 2,500,000 t/year of sugarcane, working from June to December (i.e., 6 months per year). The SCBA was then dried as per the ASTM D4442-20 standard in order to remove its moisture [52]. The dry material was subsequently sieved to remove particles that did not pass through a 12-mesh sieve (i.e., 1.7 mm diameter holes). Approximately 98% of the ash passed through the sieve. DARCO H2S activated carbon (in this work referred to as Darco AC) was provided by Cabot Norit Activated Carbon Americas Inc. (Boston, MA, USA) and was used in this work as control. Synthetic gas containing H_2S (with the following composition: 65.0% CH_4, 34.8% CO_2, 2000 ppm H_2S) was obtained from Air Liquid Compressed Gases. An additional material, rice husk ash, was employed solely for the comparison of results and to better understand the potential of other types of biomass ash for H_2S removal from biogas. Rice husk ash was obtained from a small rice mill facility in Lomas de Sargentillo (Province of Guayas, Ecuador; 1°52′59.8″ S, 80°04′41.9″ W).

2.1. SCBA Characterization

Ash content was determined following ASTM E1755-01 [53], in duplicate, after drying at 105 °C for 24 h (ASTM D4442-20) [52]. Proximate analysis was carried out via thermogravimetry, employing a Mettler-Toledo TGA/DSC 1 instrument (as per ASTM D7582-15) [54]. For the test, a constant nitrogen flow (30 mL/min) at temperatures from 25 to 600 °C and a heating rate of 10 °C/min were employed. Ultimate analysis was carried out following the process reported by [50], in triplicate, using LECO® TruSpec CHN equipment (LECO, St. Joseph, MI, USA), coupled with a LECO® 628S module. The surface area of the SCBA was assessed via gas sorption using N_2 at 77 K (−196 °C) as the adsorptive, following the procedure reported previously in [50] and employing Micromeritics ASAP 2020 equipment (Norcross, GA, USA). For the N_2 sorption tests, the samples were outgassed under vacuum conditions (i.e., at 0.5–1.0 Pa) and at a temperature of 250 °C, for 18 h. The computation of the apparent surface area followed the Brunauer–Emmett–Teller (BET) theory, which was applied to the N_2 sorption isotherms at an interval relative pressure (p/p_0) of 0.06–0.3 [55].

Scanning electron microscopy (SEM, Tescan Vega3 instrument, Warrendale, PA, USA) was employed to observe the morphology of the SCBA. The equipment, coupled with energy dispersive spectrometry (EDS), was also used to analyze the particles' surface chemical compositions. Prior to the tests, the samples were subjected to gold sputtering. Fourier transform infrared (FTIR) served to assess the functional groups on the surface of the SCBA. FTIR spectra were recorded on a Nicolet iS50 FT-IR spectrometer (Thermo Scientific, Waltham, MA, USA) equipped with Smart iTR using an attenuated total reflectance (ATR) sampling accessory. The spectra were acquired in absorbance mode in the 600–4000 cm^{-1}

wavelength range by averaging 64 scans at a spectral resolution of 4 cm^{-1}. The result was processed using OMNIC software (Version 8.0, Nicolet Instruments Corporation, Madison, WI, USA).

2.2. Biogas Scrubbing Test

The biogas scrubbing procedure and the corresponding laboratory setup have been reported in previous works [50,56]. Briefly, a polycarbonate tube (6.35 mm of internal diameter, 50 mm long) was used for the sorption process. The SCBA column in the tube contained 0.3 g of the material. The synthetic biogas was humidified using a 0.01 N HCl solution with 500 mL of distilled water; then, it was passed through the column at a rate of 10 mL/min, which was controlled using a couple of needle valves. The gas composition was continually monitored online using a gas chromatograph (GC; Varian GC3800, equipped with an Agilent CP-SilicaPLOT 50 m × 0.53 mm × 4 µm column). Measurements of the H_2S concentration in the synthetic gas were continuously conducted after the column throughout the experiment using a computer-automated data acquisition program. LC workstation version 6.30 software was used to compute the concentration of H_2S at the column's outlet. As in a previous study, the breakthrough point in the sorption isotherm was defined as the time at which the concentration of H_2S at the outlet of the column reached ~10% of the original concentration of the gas (i.e., the H_2S concentration after the column was ~200 ppm) [50]. The elemental composition of the SCBA after the scrubbing process was tested again, in triplicate, to determine its S content and, thus, to estimate the H_2S retention capacity of the SCBA. The test was replicated using the rice husk ash and the AC (used as a control). Analysis of variance (ANOVA) was conducted using OriginPro 7 (Originlab) to determine the statistical significance of the data on the S content in the adsorbent materials before and after the H_2S scrubbing tests.

3. Results and Discussion

3.1. SCBA Properties

Figure 1a shows the TG curve for the SCBA. The figure suggests that the content of volatiles in this material was very low (~2.7 wt%), as was found in previous work for a similar material [13]. Consequently, the fixed carbon content plus ash content was very high (i.e., >97 wt%). High fixed carbon is expected for some types of biochars, such as rice-straw-derived biochar [57]. For SCBA, low volatiles content is likely caused by the release of most of the volatiles from the material in the boiler's chamber due to high temperatures. The ash content was 57.9 mass%; i.e., 42.1 wt% of the SCBA was constituted by organic materials (char). Therefore, the fixed carbon content was calculated to be 39.3 wt%.

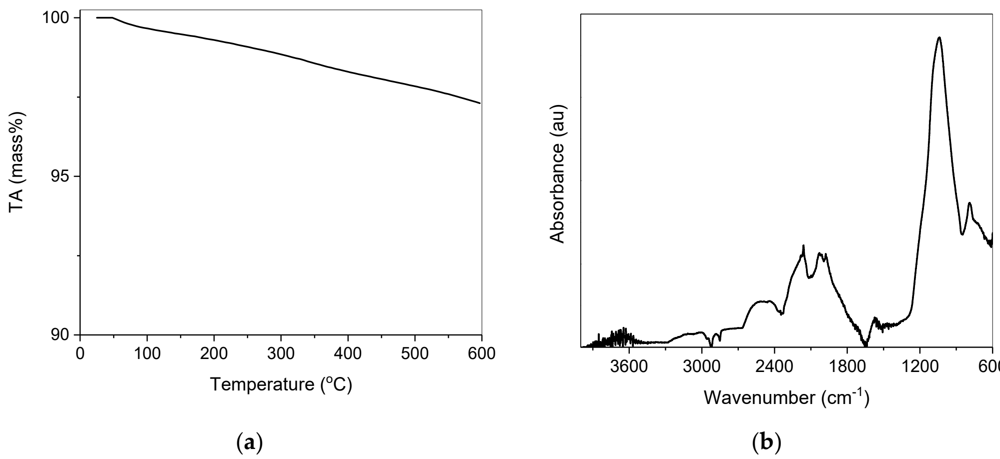
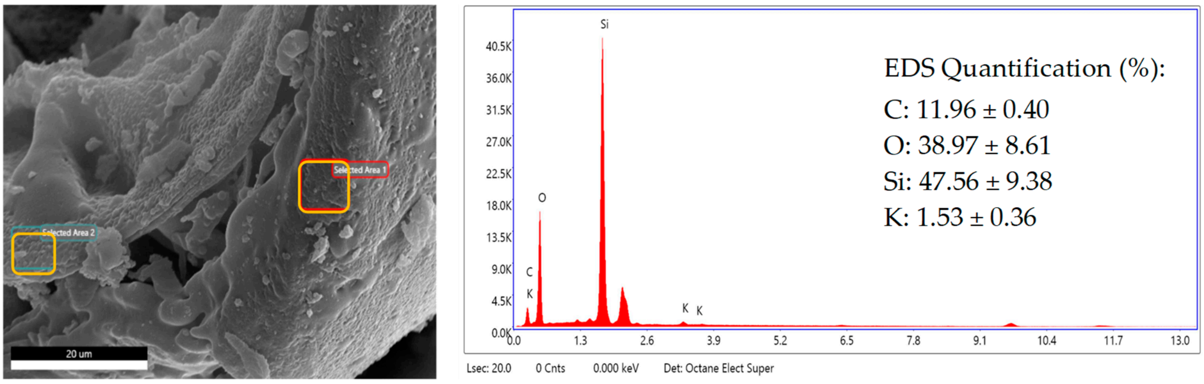


Figure 1. (**a**) TG and (**b**) FTIR curves of the SCBA used in this work.

The FTIR spectra of the SCBA are presented in Figure 1b. In the figure, strong peaks were observed at 1043 cm^{-1} and 800 cm^{-1}, which correspond to Si-O-Si and Si-O stretching vibrations, respectively. The existence of these peaks is likely due to the presence of SiO_2 and potassium silicates on the char's surface (for example, K_2SiO_3 or $K_2Si_2O_5$, since the presence of K was identified in the EDS analysis, Figure 2b). Moreover, the peaks observed at 1974 cm^{-1} can be attributed to C=C stretching in the conjugated alkenes or aromatic compounds, such as benzene rings. The other peaks in the spectrum can be ascribed to the C≡C triple bond stretching in the alkynes (2158, 2046, 2500 cm^{-1}) and C-H stretching in the aromatic compounds (2500 cm^{-1}). The absence of any significant peaks between 3200 cm^{-1} and 3600 cm^{-1} suggests a low presence of moisture on the SCBA surface. This result was expected since, as previously mentioned, the temperatures in the combustion chambers of the boilers in sugar mills are high (approximately 1000 °C and even higher) [58].



(**a**) (**b**)

Figure 2. (**a**) SEM picture of SCBA showing examples of areas selected for EDS analysis; (**b**) EDS spectrum and the corresponding surface elemental composition.

The morphology of SCBA chars and an example of the EDS spectrum of analyzed points on the surface of the SCBA particles are presented in Figure 2. The morphology of the SCBA was similar to that reported in previous works for this material [8,20,59,60]. Substantial quantities of Si were detected, besides C and O on the SCBA particles' surfaces (Figure 2b). High Si content is expected due to the high ash content in SCBA, but this element by itself has not been reported to impact chars' scrubbing capacity towards biogas. Additionally, K was the other element detected in significant proportions on the SCBA surface (Figure 2b).

The N_2 sorption isotherms of the SCBA and the control material are presented in Figure 3. The shape of the isotherm of SCBA (Figure 3a) at low relative pressure suggested a type I BET (Brunauer–Emmett–Teller) curve, with a well-defined porous structure and the presence of micropores, as confirmed by Figure 4, which shows the pore-width cumulative distribution of the SCBA. The shape of the curve in Figure 4 shows that approximately 50% of the pore width was smaller than 2 nm (i.e., there was a relatively large contribution of micropores to the total porosity of the material) and ~30% of the pore width corresponded to a mesoporous material. Thus, the BET theory was applied to determine the apparent surface area of the SCBA. The resulting apparent surface areas were 155.4 ± 0.8 m^2/g and 394.4 ± 0.8 m^2/g for the SCBA and the Darco AC, respectively. The total pore volume of the SCBA and the Darco AC were 0.1056 cm^3/g (at P/P_0 = 0.986957) and 0.4041 cm^3/g (at P/P_0 = 0.982852), respectively. As with gasification chars [50], the SCBA showed a relatively high porosity too. The maximum pore diameters were 150 nm for the SCBA and 115 nm for the Darco AC. The low hysteresis observed in the SCBA BET isotherm (Figure 3a) suggests that the material presents well-defined pores, where the gas molecules can easily enter and leave.

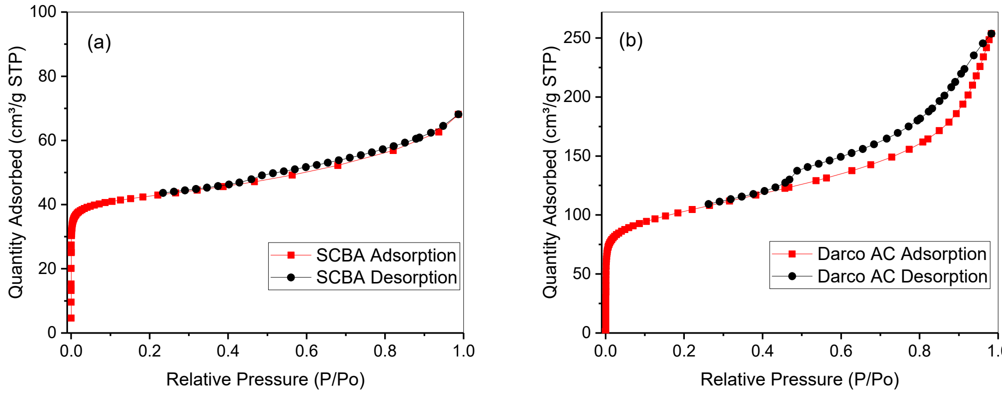


Figure 3. Sorption isotherms for (**a**) SCBA and (**b**) the AC used as control (note difference on vertical axis scale).

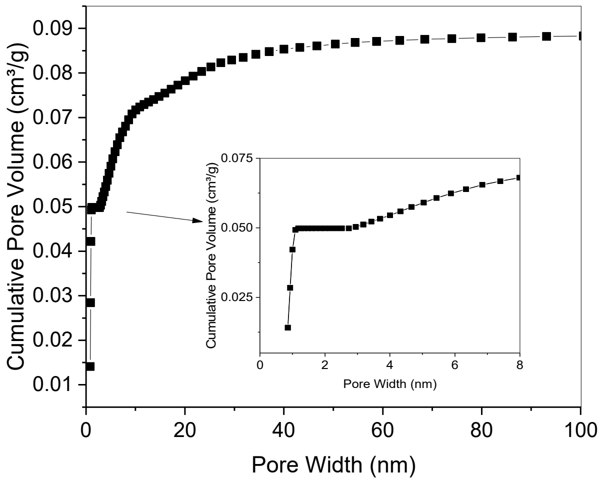
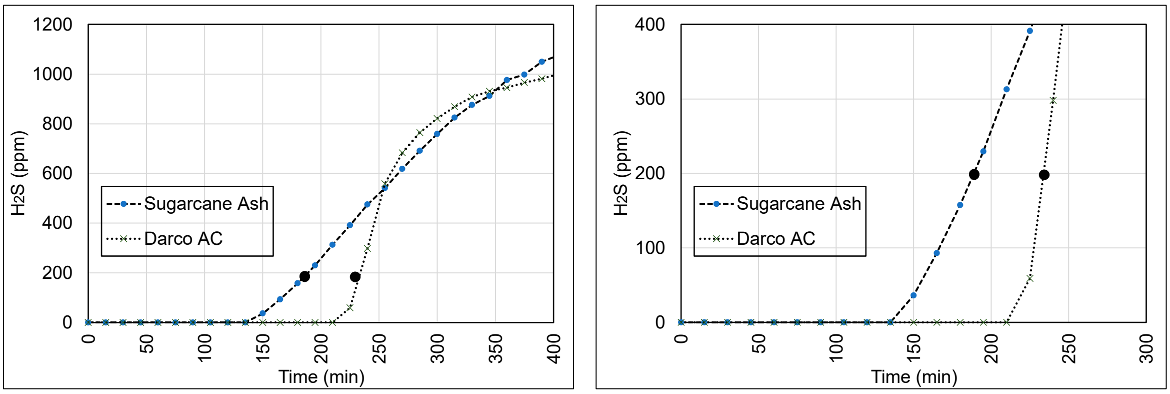


Figure 4. Pore width cumulative distribution of the SCBA.

3.2. Biogas Scrubbing Results

The behaviors of the SCBA and the Darco AC during the biogas cleaning tests are shown in Figure 5. Under experimental conditions, the breakthrough point for the SCBA was 190 min; i.e., ~75% that of the Darco AC (i.e., ~240 min), which is an excellent material for H_2S removal from biogas and serves as a reference. For comparison purposes, the breakthrough points of the gasification chars, using similar experimental conditions, was 195 min [50]. Thus, as-received SCBA's behavior was comparable to that of gasification chars, which have been identified as potential materials for H_2S removal within biogas [50,51]. This result can be explained by two factors: (a) the presence of microspores in SCBA that can facilitate the access of H_2S molecules to the external surface and inside of the pores, leading to complex adsorption behavior [61]; and (b) the presence of potassium silicates on the surface, which is equally important for the capacity of SCBA to remove H_2S from biogas. It is known that K is responsible for enhancing H_2S sorption capacity because K ions can promote the formation of catalytic centers on the chars' surfaces [62]. It is also likely that the polar nature of the Si-O and Si-O-Si bonds in silicates (such as K_2SiO_3 or $K_2Si_2O_5$) can attract polar molecules such as H_2S. Although the performance of SCBA for H_2S removal is relatively lower than that of AC designed for this purpose, its abundance in sugarcane mills and low cost makes SCBA a compelling option for biogas scrubbing, especially in countries with high sugarcane production.



(**a**) (**b**)

Figure 5. (**a**) H_2S sorption curves for SCBA and AC. The black dots display the time corresponding to the breakthrough point for each material (Figure (**b**) has been augmented for better visualization of the breakthrough point).

Tests conducted for removing H_2S from biogas using the rice husk ash (see Section 2) showed that the breakthrough point of this material was only 17 min (results not shown), which is a noticeably poor result when compared to that of the SCBA. Lack of sufficient organic material (i.e., char) in the rice husk ash explains its poor performance in removing H_2S from biogas. The inorganic content of the rice husk ash was approximately 92%, which agrees with results reported in previous works [63]. This finding suggests that not all chars obtained from lignocellulosic biomass burners (e.g., boilers) are suitable for H_2S removal from biogas. Therefore, low amounts of organic matter in combustion ashes suggest that the ashes will perform poorly in biogas scrubbing processes.

Table 1 shows the elemental composition of the SCBA and the AC used as control, before and after the biogas-cleaning test to remove H_2S. The presence of S in the SCBA and the increase in the S content in the Darco AC after the biogas scrubbing process are an indication of the H_2S retention. It is noted that the amount of H_2S retained by the SCBA is close to that retained by gasification chars, as reported previously [50].

Table 1. Elemental composition of SCBA and Darco AC before and after the H_2S removal from the biogas.

	C (Mass%)	H (Mass%)	N (Mass%)	S (Mass%)	H_2S Retention Capacity (mg H_2S/g)
SCBA before *	26.66 ± 1.05 **	0.57 ± 0.07	0.31 ± 0.02	0 **** (A) *****	
SCBA after	21.98 ± 0.09	0.52 ± 0.01	0.22 ± 0.01	1.35 ± 0.01 (B)	~17.41
Darco AC before	52.68 ± 2.62 ***	0.65 ± 0.02	0.56 ± 0.06	0.53 ± 0.04 (C)	
Darco AC after	52.01 ± 2.59	0.64 ± 0.02	0.55 ± 0.06	1.89 ± 0.07 (D)	~20.35

* Before the biogas cleaning test. ** Oxygen and other elements in ash complete the elemental composition balance of SCBA. *** Oxygen completes the elemental composition balance of Darco AC. **** Out of limit of detection. ***** Values with different letters indicate significant differences at the α = 0.05 level.

3.3. Possibility of Integrating Biogas Production from Vinasses with Biogas Scrubbing Using SCBA

In ethanol-producing sugarcane mills, biogas production is expected to increase in coming years due to the necessity of the better management of vinasses. Currently, vinasses are the largest source of contamination in ethanol production from sugarcane [46]. The vinasse stream is acidic (pH 3.5–5), with a high organic load (chemical oxygen demand up to 140 g/L) and a relatively low concentration of nutrients (e.g., up to 4.3 g/L of nitrogen, up to 3.0 g/L of phosphorous, and/or up to 17.5 g/L of potassium) [64]. Vinasse is used in some countries as a fertilizer in sugarcane plantations, but the economical transportation of vinasses is restricted to short distances from sugarcane mills. The average radius of economically viable vinasse application in natura is 11 km from the sugarcane mill, which can be increased up to 29 km if vinasse concentration steps are carried out [65]. The direct use of this material as a fertilizer can also be restricted in some types of soils due to the soils' salinity [49]. In some places, vinasse is discharged in water bodies [49], which may require the depollution of this effluent before its release into nature [64]. Thus, biogas production is the most developed and economically viable method currently available for vinasse treatment [49,64,65]. The integrated use of vinasses and SCBA appears promising for better management of these residues.

Many countries worldwide are highly dependent on crop production for both exporting and domestic consumption. For example, in Ecuador, the three most grown crops are banana, rice, and sugarcane (6.6, 9.3, and 1.1 Mt/year, respectively, in the year 2019) [66]. The main method employed to increase the fertility of the soil used for these crops is through the addition of N-based synthetic fertilizers, especially urea. However, it is known that N-based fertilizers promote soil acidification [67–70]. The pH in some soils in Ecuador are as low as 5 [71], which, in part, results from the use of synthetic fertilizers. The soil acidification process is largely responsible for decreasing crop yields. In Ecuador, the sugarcane yield decreased from 79 to 70 t/ha from 2014 to 2019 [66]. Although there are options for increasing soil pH, the use of charcoal (referred to as biochar) has been proposed as a promising method for this purpose [72]. The sulfur-rich SCBA obtained after a biogas scrubbing process could positively impact soil quality and the growth of plants [73]. Currently, commercial fertilizers contain large amounts of sulfur, either as sulfate or elemental S [74]. Therefore, S-enriched SCBA (after the biogas cleaning operation) is expected to be more beneficial to soils than directly using the ash, thus adding value to this material. The integration of SCBA with biogas production and cleaning can improve the sustainability of the sugarcane industry through better management of the residues. In addition, the use of as-received SCBA for biogas cleaning is beneficial as this material does not require a preparation process as in the case of devoted adsorbing materials for biogas scrubbing. Further work should assess the potential of SCBA for simultaneous CO_2/H_2S removal and, expectedly, the use of this type of ash for soil fertilization and complementary carbon sequestration. The possibilities of using other types of combustion ashes for CO_2 removal from biogas have been proven successful in previous works [75].

4. Conclusions

As-received sugarcane bagasse ash obtained from a sugarcane mill was used to remove hydrogen sulfide from biogas. It was found that the SCBA's capacity to remove H_2S from biogas was approximately 75% the capacity of specialized activated carbon. SCBA's ability to remove H_2S from biogas is comparable to the capacity of chars obtained from biomass gasification plants reported in the literature. This result was attributed to the relatively high amounts of microporous organic material (char) and the presence of K compounds on the SCBA's surface. The implications of these findings are pertinent to the sugarcane agroindustry, especially for purifying biogas generated from vinasses prior to its in situ utilization, where economic considerations may limit the use of specialized activated carbons or alternative biogas scrubbing processes. The integration of biogas production and cleaning operations using abundant, locally available residues generates new approaches for making the sugarcane industry more sustainable. Additionally, the potential of sulfur-enriched SCBA, postbiogas cleaning, holds greater promise compared to the direct application of this material for soil fertilization, as sulfur is an essential nutrient for the growth of plants.

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