Filter Performance in the Reduction of Hydrogen Sulfide in Biogas

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Abstract— *The objective of this study was to verify the efficiency of filters in reducing the concentration of hydrogen sulfide (H_2S) in biogas. In this case, adsorbent calcined clay and commercial activated charcoalwere employed, both with chemical activation utilizing ferric chloride. The filters were compared with iron filings with the values obtained for standard filters. The experimental design was completely randomized, with six treatments and three replications. The treatments consisted of the collection of H_2S present in biogas generated in a biodigester without filtration (control), with an iron filter (ERBR®), with filters formed by calcined clay with and without impregnation by iron, and commercial activated charcoal with and withoutiron impregnation. The adsorbents were characterized in relation to the crystalline or amorphous phases present determined by X-ray diffractometry, the specific surface area, volume and distribution of pore size, and tests of adsorption isotherms in blue methylene. The commercial activated charcoal filter with iron impregnation was the most efficient in the removal of hydrogen sulfide from biogas. Its superior performance with a higher adsorption capacity is due to the large specific surface area of activated charcoal, as well as the chemical interaction between H_2S and iron ions impregnated over coal.*

Keywords— *commercial activated carbon filter, calcined clay filter, iron mesh filter.*

I. INTRODUCTION

The agricultural and industrial technology revolutions have transformed how we live, enabling a growing percentage of the world's population to heat and illuminate their homes, to be more connected globally with advancements in transportation, and to more productively fertilize and irrigate their crops. This progress has been fueled by the ability to effectively locate, extract, and use energy with increasing ingenuity. Materials science research continues to pursue sustainable solutions that contribute to achieving technically- and economically-feasible clean energy generation, transmission, distribution, and storage, with greater energy efficiency, and improved energy management systems [1].

According to the Brazilian Energy Research Company (EPE), in 2016 renewable energy accounted for 43.5% of the nation's total domestically-produced energy supply, while the world average was around 14%, with only about 6% in developed countries. This 43.5% encompassed17.5% sugarcane biomass, 12.6%

hydropower, 8% firewood and charcoal, and 5.4% from other sources including 0.9% from biogas[2].

Anaerobic digestion is a biological process that can convert organic substrates into biogas in the absence of oxygen. The anaerobic digestion process generates a series of compounds. Among them is hydrogen sulfide (H_2S), which is useless for energetic purposes [3].

H_2S is a flammable gas, denser than air, with an unpleasant odor, toxic to humans, and caustic. It corrodes critical engine components, negatively impacting power generation, and must be extracted to enhance biogas quality. The recommended level of H_2S in biogas for direct combustion is in the range of 0.02% to 0.05% (200 to 500 ppm). Therefore, desulfurization is necessary to protect the combustion equipment from damage and prevent the formation of sulfur dioxide (SO_2), which is a precursor of acid rain. The removal of H_2S from biogas is commonly accomplished with the use of filters [4, 5].

A review of the literature revealed multiple applications and approaches for the removal of H_2S being investigated in recent years including the study of

anaerobically digested fiber charcoal for H_2S removal in biogas by Pelaez-Samaniego et al. [6], the removal of H_2S from biogas involving the anaerobic fermentation of swine manure using iron oxide, calcium hydroxide, and charcoal verified by Machado et al. [7], and, in the investigation of biogas purification from household waste, Ebunilo et al. [8] used materials found in Nigeria, including charcoal, potash, clay, iron ore, and zeolite, as filter elements.

Since at the small scale the cost of using commercial filter media based on iron or carbon to remove H_2S can act as a barrier to the adoption of biogas technology on the farm, Skerman et al. [9] , seeking low-cost filtering media, studied a red soil filter for its potential to remove H_2S present in standard gas. And in one review focused on nanoporous materials, such as H_2S adsorbents for biogas purification processes, Peluso et al. [10] asserted that activated charcoals have been studied extensively for many years in this application, providing good results, although they have limited regenerability.

The mesoporous silicas ordered with amino function produced very interesting results, both in terms of adsorption performance and regenerative capacity, but were not tested on a large scale and deserve further investigation. On the contrary, despite reporting very good results, there are few studies dealing with the adsorption of H_2S in organic structures of nanoporous metal. Thus, the objective was to verify the efficiency of filters that incorporate calcined clay and activated charcoal impregnated with iron ions for the reduction of hydrogen sulfide (H_2S) in biogas.

II.   MATERIAL AND METHODS

Initially, we proceeded to characterize the materials used as adsorbents (calcined clay-CC and commercial activated charcoal-CAC). As a reference in gas filtration, the characterization of the specific surface area, volume, and pore size of the calcined clay and commercial activated charcoal was performed. For this analysis, the samples were subjected to drying and cleaning of their surfaces by heating at 200 ° C for 3 hours under vacuum in the degasser system. After this operation, the samples were analyzed for the gaseous nitrogen physisorption isotherms (N_2) at the liquid N_2 temperature (77 K) in a Quantachrome Instruments®model NOVAtouch LX2. The obtained isotherms were treated with the appropriate mathematical models to obtain the information of interest.

For the qualitative analysis of phases present in the adsorbents, the X-ray diffractometry technique was used, where the samples were prepared with the maceration of the material to obtain a fine powder, and deagglomerated

in a 325 mesh sieve (opening 45 μm). The diffract grams were collected in continuous scanning mode in an X-ray diffract meter, model XRD-6000 (Shimadzu), equipped with a graphite-curved monochromatic and copper anode, with Kα radiation (1, 54060Å). The equipment was operated at 40 kV and 30 mA, with divergence and dispersion cracks of1.0 ° and a receipt slit of0.3 mm. The analysis was performed with a $2min^{-1}$ scanning speed on the theta-2theta movement axis.

In iron impregnation, the materials were placed in a 0.5 mol L^{-1} iron nitrate solution. A 0.8 g mL^{-1} adsorbent ratio was used in relation to the iron ion solution. The mixture was under agitation for 3.0 h at 300 rpm in a mechanical agitator Fisatom until impregnation occurred. After the elapsed time, the modified adsorbents with iron were filtered, dried in a greenhouse for 12h to 100 ° C, and stored in a desiccator until the filters were assembled. This step was performed to increase the adsorption efficiency of H_2S by chemical interaction with iron ions.

The adsorbents, pure and adsorbed with iron ions, were characterized by isotherms in methylene blue solution, where 1.0 g of each adsorbent was used (calcined clay, calcined clay impregnated with iron, commercial activated charcoal, and commercial activated charcoal impregnated with iron). The adsorbents were added in vials containing methylene blue solution at different concentrations (10, 25, 50, 100, 250, 500 and 1000 mg L^{-1}). The adsorbents were in contact with the solution in static mode for 24 hours at room temperature. The remaining concentrations of methylene blue were analyzed in a Varian Cary 50 UV-Vis spectrophotometer at 660 nm. The number of methylene blue was defined based on the Langmuir isotherm, plotting EQF (mg G^{-1}) as a function of the methylene blue concentration in the equilibrium time. The parameters of the Langmuir isotherm (Qmax and KL) were found by regression of the quadratic equations.

The preparation of the filters occurred in the laboratories of the State University of Ponta Grossa (PR-Brazil) in 2018. To assemble the filters, each adsorbent material (calcined clay and commercial activated charcoal, pure and activated with iron) was placed inside a closed PVC container where covers with copper tubes were adapted for gas passage. The established mass of each adsorbent was 10.0 g per filter (Figure 01).

The efficiency of the filters was evaluated in-situ at the farmVale do Jotuva® (Carambeí, Paraná, Brazil), with biogas generated by abiodigester (ERBR®-Canadian model) using milk cattle residue. The filters were installed in a biogas-driven electric motor-generator in conjunction with agas suction pump (Electric Air Pump®-2021/127) for a constant flow of 7.0 L min^{-1}, and anH$_2$S meter (Gas Clip

Technologies®-SGC H_2S). To quantify the volume of gas that passed through the filter, a Protec® Flowmeter was used with a capacity of 15 L min^{-1} (Figure 02). The concentration of H_2S was measured 1.0 m after the filter for a period of 60 minutes of gas passage through the filters.

The experimental design was completely randomized, with six treatments and three replications. The treatments consisted of a control (no filter for H_2S reduction), a standard iron filter (ERBR®), calcined clay (with and without iron adsorption), and commercial activated charcoal (with and without iron adsorption). The repetitions were composed of three filters for each treatment.

The values recorded were analyzed by Hartley's test to verify the homoscedasticity of the variances, and by the Shapiro-Wilk test to examine the normality of the data. The variables measured were subjected to analysis of variance by the Fisher-Snedecor test, and the mean values compared by Tukey's test, with a confidence level higher than 95% of probability (P < 0.05).

III.   RESULTS AND DISCUSSION

The specific surface area (BET) was 1.5 m^2 G^{-1} for calcined clay, a value much lower than the 817 m^2 G^{-1} of commercial activated charcoal. Pore volume (BJH) was 0.0004 and 0.0459 (cm3 G^{-1}) for calcined clay and commercial activated charcoal, respectively. The pore radius (BJH) was similar among the evaluated materials, being 1.66 and 1.67 (nm) for calcined clay and commercial activated charcoal, respectively. The clay was calcined at high temperatures (1300 °c),which did not contributetointerlamellar porosity as in activated charcoal, and which isonly due to theexternal surface area of the particles.

Utilizingthe X-ray diffractometry technique, the presence of crystalline phases in the adsorbents was qualitatively identified. There was observed in the diffractogram of calcined clay (Figure 03-A) several diffraction peaks identified as cristobalite (SiO_2), quartz (SiO_2), and mullite ($3Al_2O_3.2 SiO_2$). Also observed was a region of amorphous material, probably referring to some phase of SiO_2, not crystallized. For commercial activated charcoal (Figure 03-B), a diffraction pattern was observed identified as the graphite crystalline phase (C) - that is, a more organized charcoal - confirming its larger surface area. Some silica-related diffraction peaks were identified. A pattern of amorphous material was also observed, referring to the disorganized carbon phase, not yet fully converted to graphite.

For the characterization of adsorbents by methylene blue adsorption isotherms, the standard curve for concentrations by molecular absorption spectrophotometry in the UV-Vis region was determined. Methylene blue adsorption isotherms are shown in Figure 4.

The values of the Qmax and KL parameters of the Langmuir isotherm (Table 01) establish the maximum value in milligrams of dye that the adsorbent is capable of adsorbing per gram, highlighting large differences between the tested materials. Thus, the adsorbent capacity (Qmax) of commercial activated charcoal is 4.4 times greater than the calcined clay. This is directly related to the large specific surface area of activated charcoal observed in the N_2 physisorption. The impregnation with iron (adsorption) reduces the adsorption of methylene blue dye in both adsorbents since the active sites are occupied with iron ions.   For the adsorption of H_2S, the adsorbents impregnated with iron should be potentialized since chemical adsorption of H_2S can occur at sites occupied byiron ions.

The Hartley's test to verify homoscedasticity, and Shapiro-Wilk to examine the normality of the data, were not significant; thus, not requiring data transformation or analysis of variance. With the significance of the Fisher-Snedecor test, the retention of H_2S by Tukey was compared (Table 2).

When the adsorbents studied wereapplied in the production of biogas filters, it wasobserved that the concentration values of H_2S reached the limit of the reading of the apparatus for the control treatments (without filter) and iron filings (standard). Subsequently, the H_2S retention sequence by the filters was inthe following ascending order: calcined clay, commercial activated charcoal, calcined clay adsorbed with iron, and commercial activated charcoal adsorbed with iron. These values confirm the previous analyses of specific surface area and adsorption of methylene blue.

The results obtained in the present study do not confirm the conclusions of Pelaez-Samaniego et al. [6]. The authors concluded that the coal capacity obtained from anaerobically digested fibrous solids for H_2S removal is comparable to that of activated charcoal. The retention of H_2S is in consonance with the calculation of the Qmax parameter of the Langmuir isotherm. For the adsorption of methylene blue, the higher the determined value, the more methylene blue adsorbed on the material. Thus, the efficiency of commercial coal proved to be greater than that of clay. The iron impregnation in the adsorbents improved the adsorption of H_2S, as discussed, in the adsorption isotherm of methylene blue.

The results obtained in this study corroborate the investigation by Machado et al. [7], as they conclude that the serial treatment (filtration by iron oxide, calcium hydroxide, and charcoal) is optimal for the removal of H_2S and CO_2 (53.5%).

The H_2S reductions in the biogas of this assay were higher than obtained by Ebunilo et al. [8] using materials found in Nigeria as a filter element. In this African country, the best result was obtained with afilter consisting of amixture of the materials clay, iron, coal, potassium and zeolite, which reducedH_2S in biogas to 0.01%.In Brazil, the reduction of H_2S in biogas was reduced further to0.0028% with the commercial activated carbon filter adsorbed with iron.

The clay and activated charcoal filters tested appear to be more promising than those investigated by Skerman et al. [9] when searching for low-cost filter media. In that work, the red soil filter was the most promising alternative medium, yet far below the ideal, removing only 5% of the H_2S present in standard gas. These filters maintained H_2S at recommended levels of use for direct combustion [4 and 5]. In the present work, the treatments that cannot be confirmed to have maintained the recommended level of H_2S in biogas for direct combustion were the control (without filter) and the iron filter (standard).

Thus, it follows the contribution to progress towards a sustainable future [1], since the supply of renewable energy sources has great potential for expansion [2]. The ability to withdraw hydrogen sulfide (H_2S), present in biogas generated by anaerobic digestion, is problematic for energetic purposes [3, 4 and 5]. It is emphasized the importance of studying alternatives that deal with the adsorption of H_2S in organic structures, by the few studies focused on this objective, as highlighted by Peluso et al. [10] in review on the subject. Thus, the clay and activated charcoal filters produced in this work were prominent to solve this problem.

IV. CONCLUSION

The commercial activated charcoal filter with iron impregnation was the most efficient in the removal of hydrogen sulfide from biogas. Its superior performance with a higher adsorption capacity is due to the large specific surface area of activated charcoal, as well as the chemical interaction between H_2S and iron ions impregnated over coal.

REFERENCES

[1] Chu, S.; Cui, Y; Liu, N. (2017).The path towards sustainable energy. Nature Materials, 16, pp. 16-22. https://dx.doi.org/10.1038/nmat4834

[2] EPE - Empresa de PesquisaEnergética (2017). Balançoenergéticonacional. Available at: <http://www.epe.gov.br/sites-pt/publicacoes-dados-abertos/publicacoes/PublicacoesArquivos/publicacao-46/topico-81/S%C3%ADntese%20do%20Relat%C3%B3rio%20Final_2017_Web.pdf>. Accessed: 14 March 2019.

[3] Zhang, Q.; Hu, J.; Lee, D.J. (2016). Biogas from anaerobic digestion processes: Research updates. Renewable Energy, 98, pp. 108-119. https://doi.org/10.1016/j.renene.2016.02.029

[4] Tilahun, E.; Bayrakdara, A.; Sahinkaya, E.; Çalli, B.(2017).Performance of polydimethylsiloxane membrane contactor process for selective hydrogen sulfide removal from biogás.Waste Management, 61, pp. 250-257. https://doi.org/10.1016/j.wasman.2017.01.011

[5] Khoshnevisan, B.; Tsapekos, P.; Alfaro, N.; Díaz, I.; Fdz-Polanco, M.; Rafiee, S.; Angelidaki, I. (2017). A review on prospects and challenges of biological H_2S removal from biogas with focus on biotrickling filtration and microaerobic desulfurization. Biofuel Research Journal, 4, pp. 741-750. https://doi.org/10.18331/BRJ2017.4.4.6

[6] Pelaez-Samaniego, M.R.; Smith, M.W.;Zhao, Q.;Garcia-Perez, T.; Frear, C.;Garcia-Perez, M. (2018). Charcoal from anaerobically digested dairy fiber for removal of hydrogen sulfide within biogas. Waste Management, 76, pp. 374-382. https://doi.org/10.1016/j.wasman.2018.03.011

[7] Machado, N.S.; Silva, J.N.; Oliveira, M.V.M.; Costa, J.M.; Borges, A.C. (2015). Remoçãodo sulfeto de hidrogênio do biogás da fermentação anaeróbia de dejetos de suínos utilizando óxido de ferro, hidróxido de cálcio e carvão vegetal. Revista Energiana Agricultura, 30, pp. 344-356. https://doi.org/10.17224/EnergAgric.2015v30n4p344-356

[8] Ebunilo, P.O.; Orhorhoro, E.K.; Adegbayi, O.A. (2016). Investigation of the purification of biogas from domestic wastes using local materials in Nigeria. International Journal of Scientific & Engineering Research, 7, pp. 505-515.

[9] Skerman, A.G.; Heubeck, S.; Batstone, D.J.; Tait, S. (2017). Low-cost filter media for removal of hydrogen sulphide from piggery biogas. Process Safety and Environmental Protection, 105, pp. 117-126. https://doi.org/10.1016/j.psep.2016.11.001

[10] Peluso, A.; Gargiulo, N.;Aprea, P.;Pepe, F.;Caputo, D.(2019)Nanoporous materials as H_2S adsorbents for biogas purification: a review. Journal Separation & Purification Reviews, 48, pp. 78-89. https://doi.org/10.1080/15422119.2018.1476978
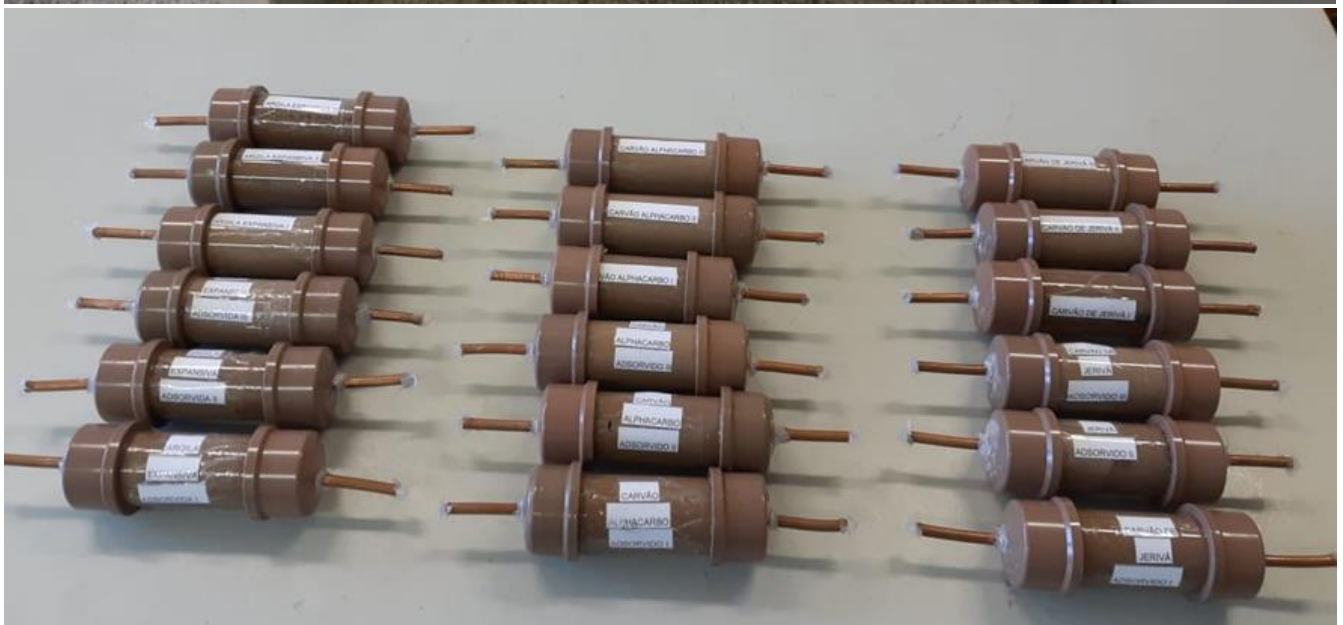
Fig.1:Filters for removal of H₂S in gas produced by biodigester fed with residue of bovinoculture, State University of Ponta Grossa, Ponta Grossa (PR-Brazil), 2018.
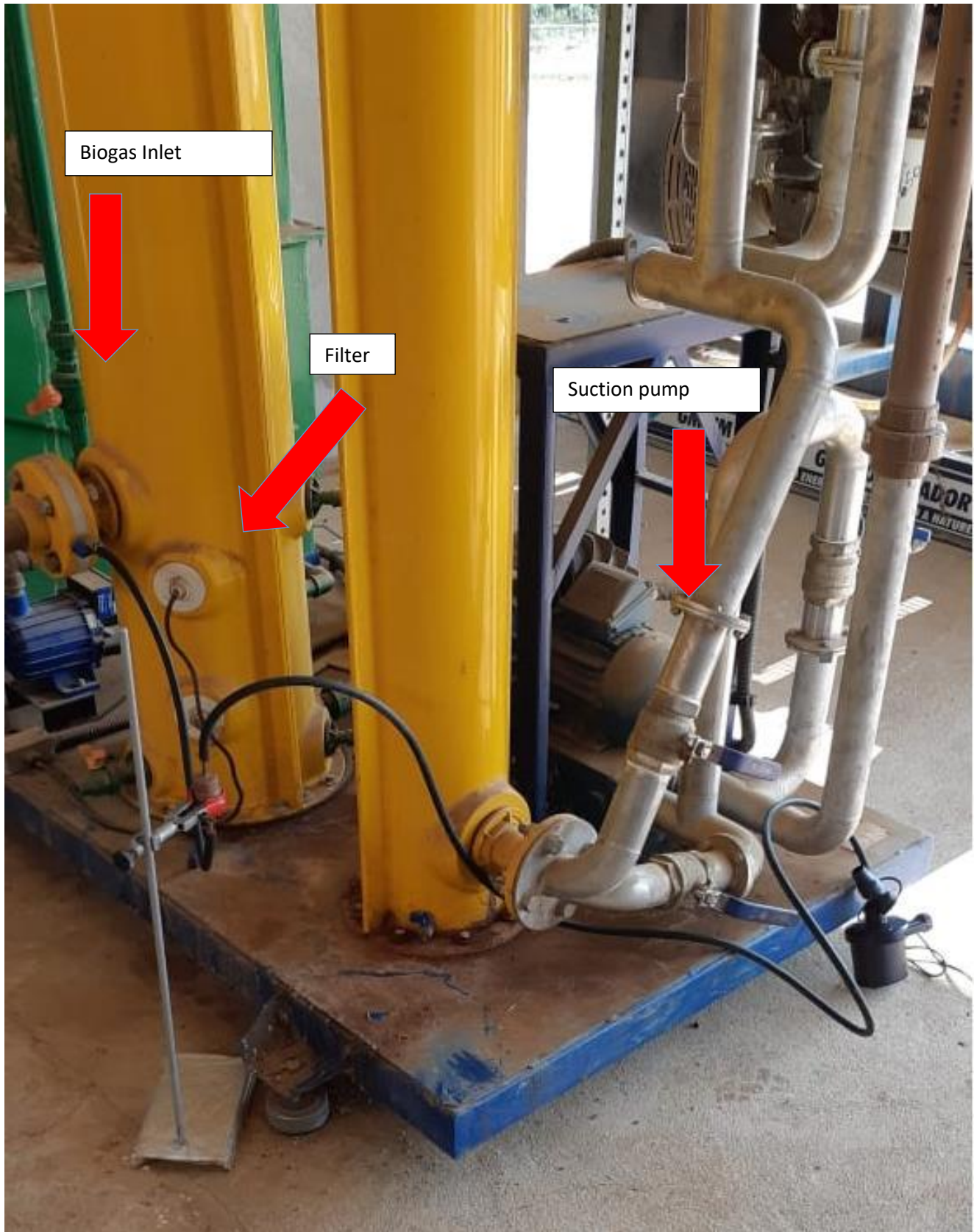
Fig.2: System assembled with the filter and the pump to keep the biogas passage in a constant flow, Carambeí (PR – Brazil), 2018.
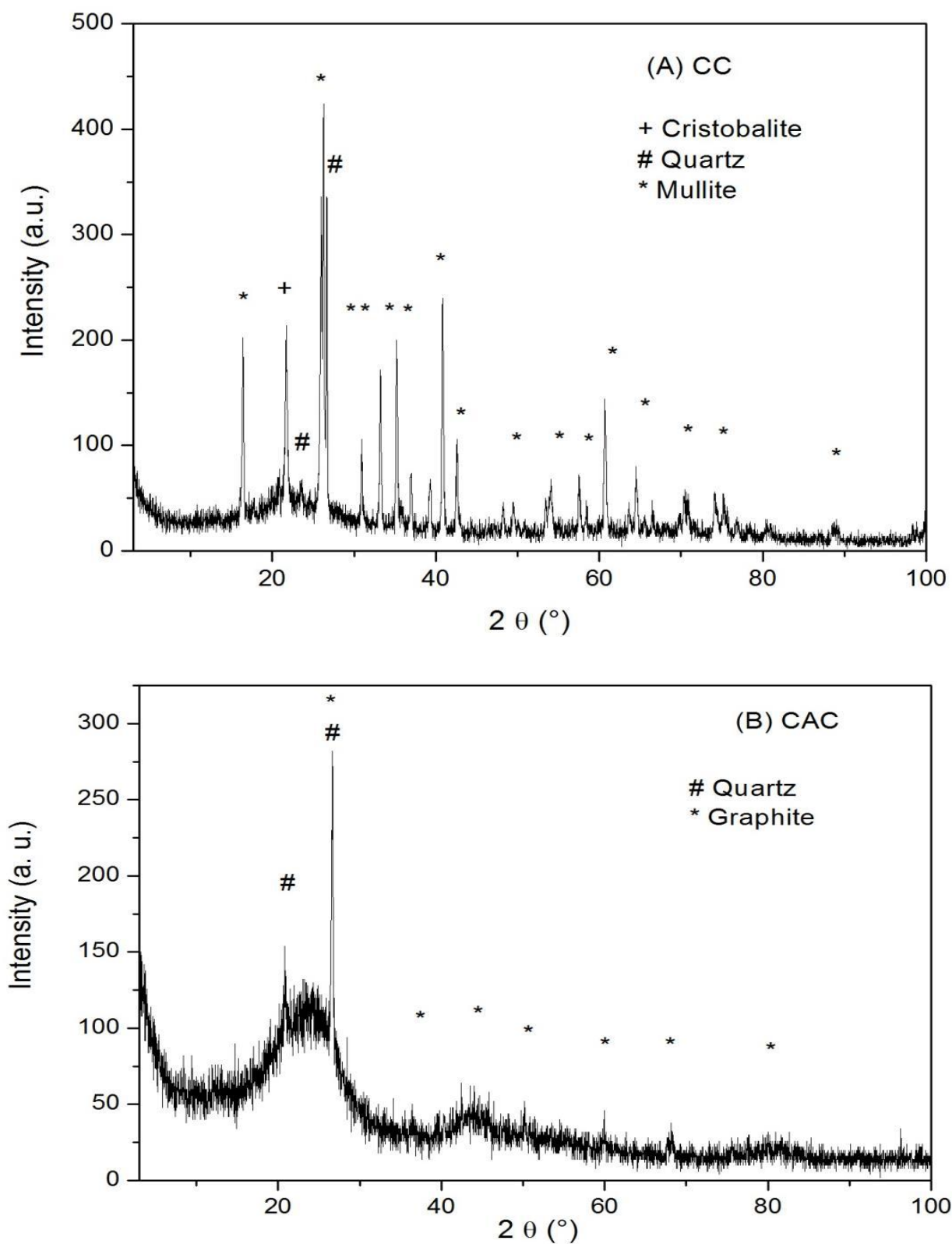
Fig.3: Calcined clay diffractogram (A) and commercial activated charcoal (B), State University of Ponta Grossa, 2018 (Brazil).
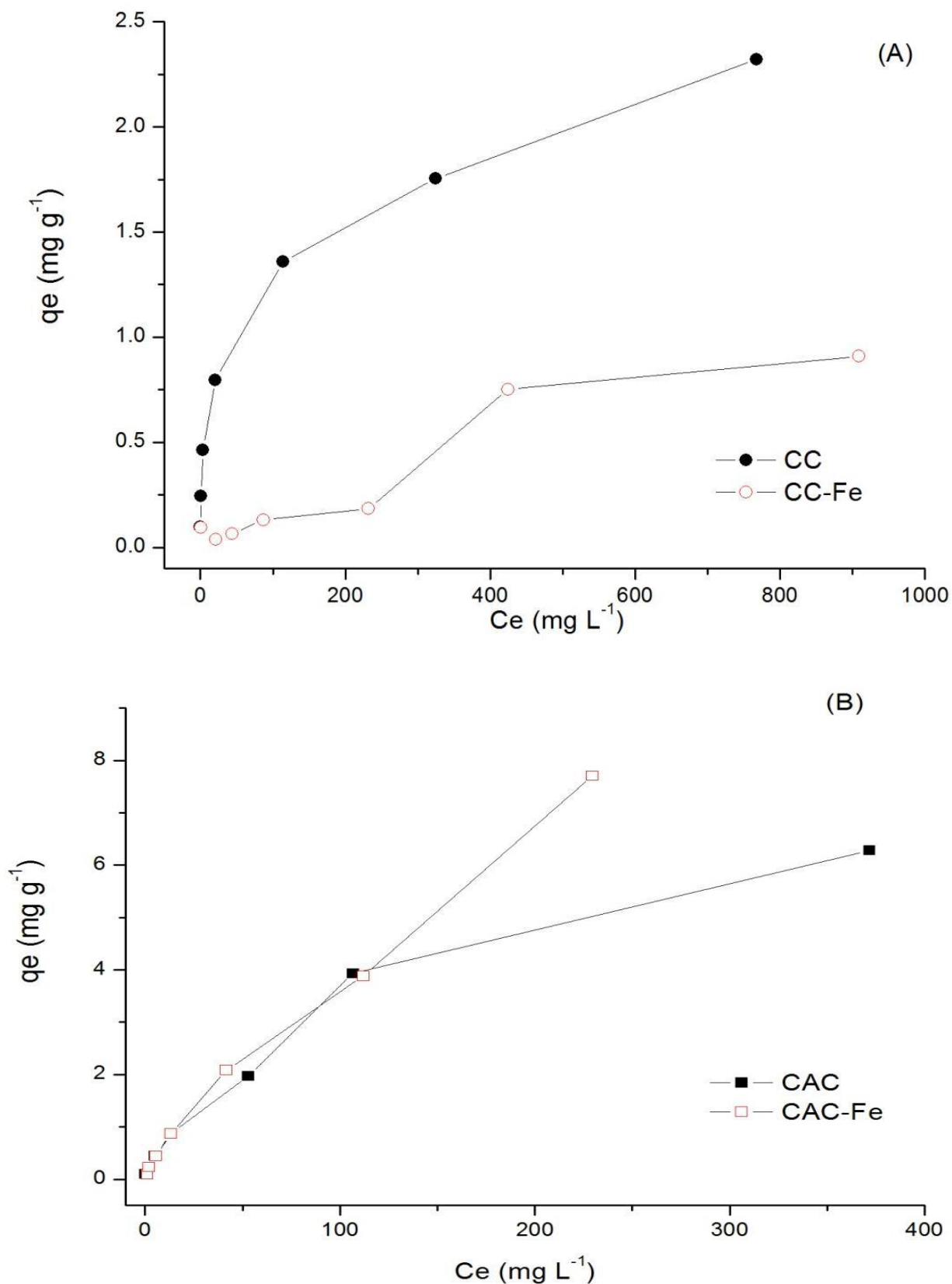
Fig.4:Adsorption isotherms of methylene blue solution for calcined clay (A) and commercial activated charcoal (B), adsorbed (with iron impregnation) or not, State University of Ponta Grossa, 2018 (Brazil).

Table.1: q_{max} and KL values obtained from the adsorption isotherms of methylene blue, according to the Langmuir model, for adsorbent materials used as filters for the reduction of H_2S in biogas, State University of Ponta Grossa, 2018 (Brazil).

Adsorbents	q_{max}[1] (mg g^{-1})	K_L[2] (L mg^{-1})
Calcined clay	0.6828	7.7138
Calcined clay adsorbed with Iron	0.1050	12.5901
Commercial activated charcoal	18.5620	0.4545
Commercial activated charcoal adsorbed with Iron	11.3084	0.008

1-q_{max} are maximum adsorption values per gram of adsorbent material.

2 – KL corresponds to the interaction constant adsorvate/adsorbent.

Table 2 - Quantity of H_2S in parts per million (ppm), determined after passage of biogas generated by biodigestion of residue from dairy cattle by different types of filters coupled in a gaseous circuit, for 1 hour, 2018, Carambeí (Paraná – Brazil).

FilterMaterials	H_2S (ppm)
Control (without filter)	100 A[1]
Iron mesh filter (standard)	100 A
Calcined clay	95 B
Calcined clay adsorlife with iron	62 D
Commercial activated charcoal	67 C
Commercial activated charcoal adsorbed with iron	28 E
Coefficient of variation	1.9 %

1-averages followed by the same letter in the column do not differ by the Tukey's test (P > 0.05).