

Analysis of copper corrosion by biogas: impact of purification with activated carbon and biochar derived from cocoa pod waste

ABSTRACT

In the context of reducing greenhouse gas emissions, this study evaluates copper corrosion in contact with biogas before and after purification using different carbons (biochar and activated carbon). Biogas, a renewable energy source, contains impurities such as hydrogen sulfide (H_2S), which accelerate the corrosion of metals, particularly copper. The materials used include carbons derived from cocoa pod waste, subjected to carbonization and chemical activation treatments. **The results indicate that biogas purification significantly reduces copper corrosion, with mass loss decreasing from an average of 0.19 g to 0.03 g after 720 hours of exposure.** Factorial designs were employed to assess the influence of various factors on the corrosion rate. **Activated carbon was found to be 85% effective in removing H_2S , outperforming biochar, which achieved a 72% removal efficiency.** In conclusion, using carbons derived from agricultural waste to purify biogas emerges as a promising solution for extending the lifespan of metallic infrastructures, with positive economic and environmental implications.

Keywords: Corrosion; Biogas; Purification; Activated Carbon; Biochar

1. Introduction

In a global context where reducing greenhouse gas emissions and combating climate change are critical, the transition to renewable energy is a key priority [1, 2]. Among these renewable sources, biogas stands out for its potential to significantly contribute to a greener, more sustainable economy while offering versatile applications [3]. Produced through the anaerobic decomposition of organic materials such as agricultural waste, food residues, and wastewater, biogas can be utilized for electricity generation, heating, or even as a transportation fuel [4]. However, its use poses both technical and environmental challenges.

One of the primary challenges is the presence of impurities, particularly hydrogen sulfide (H_2S), which causes rapid corrosion of metallic equipment, such as pipelines and distribution systems [5, 6]. This issue is especially concerning for metals like copper, commonly used in biogas infrastructure. Raw biogas, as produced by biodigesters, contains impurities like H_2S , which, due to its toxicity and corrosive nature, accelerates the degradation of infrastructure [5]. Dissolving in water present in biogas, H_2S forms weak acids that attack metals, thereby reducing their lifespan [5].

Metal corrosion, a material degradation process resulting from chemical or electrochemical reactions with the environment, is a significant concern in the biogas context [6]. Composed primarily of methane (CH_4) and carbon dioxide (CO_2), biogas also contains trace gases such as H_2S , ammonia (NH_3), and nitrogen oxides (NO_x), which exacerbate the risk of corrosion for metal infrastructure [5]. Copper, while valued for its conductivity and corrosion resistance under typical conditions, is particularly vulnerable in aggressive environments containing H_2S [7]. H_2S can lead to severe corrosion, compromising the reliability and durability of biogas systems [8].

Numerous studies have investigated biogas-induced corrosion and strategies for its mitigation, focusing on materials and protective measures. These investigations have identified potential solutions to extend the lifespan of metal infrastructure exposed to biogas [9-12]. For instance, research shows that copper and carbon steel are particularly susceptible to H_2S -induced corrosion, whereas stainless steel and aluminum exhibit better resistance [13].

Protective coatings, such as epoxy and zinc or nickel-based metallic coatings, have proven effective in reducing corrosion [14]. Nickel plating, in particular, offers excellent resistance in H_2S -containing environments, though its high cost limits widespread use [13]. Corrosion inhibitors, especially those based on thiols and phosphates, have also shown promise in protecting metals [15-17]. Additionally, approaches to minimize direct contact between

biogas and vulnerable metal components, such as using non-metallic conduits or filtration systems, are gaining traction [18].

By eradicating H₂S and other harmful substances, natural adsorbents such as activated carbon and biochar offer an ecological alternative for biogas purification [19]. Activated carbon, with its high surface area and porosity, is particularly effective, though it requires frequent replacement due to rapid saturation [19]. Biochar, produced via biomass pyrolysis, offers a more economical and sustainable solution, especially in developing countries [19]. Its performance can be optimized by adjusting pyrolysis conditions, making it a promising material for biogas purification [19].

The use of cocoa pod husks, an abundant agricultural waste, to produce activated carbon and biochar represents an innovative and sustainable approach [20]. These locally manufactured materials not only valorize agricultural waste but also reduce costs and environmental impact [20]. Furthermore, products derived from cocoa pod husks, such as activated carbon, have growing international demand, strengthening the economies of cocoa-producing countries [21].

Our study, conducted at FONDATION BRIN SARL, a poultry farming company in Côte d'Ivoire (Photo 1), focused on evaluating the corrosive effect of biogas on copper before and after purification. The primary objective of this study was to compare the corrosive impact of biogas on copper before and after purification. **The study specifically sought to:**

Assess the efficiency of activated carbon, prepared from cocoa pod husks activated with KOH, and biochar produced from the same waste as adsorbents for biogas purification.

Analyze the reduction in copper corrosion rates following biogas purification.

SIGNIFICANCE

These efforts aim to provide accessible and cost-effective solutions to enhance the durability of biogas infrastructure while valorizing local resources. The results of this study contribute to the development of sustainable technologies that support economic and environmental objectives.



Photo 1: Methanizer at FONDATION BRIN poultry farming company

The photograph illustrates the key components of the biogas system installed at Fondation Brin. The labeled features include: 1-Manual Feeding Pit: Used for the manual introduction of organic materials into the system; 2-Mechanical Feeding Tower: Facilitates the automated feeding of organic materials into the digester; 3-Anaerobic Digester: The core unit where organic matter undergoes anaerobic decomposition to produce biogas; 4-Expansion Pit: Handles overflow and expansion of the digested material; 5-Digestate Storage Basin: Collects and stores the digestate, which can be used as a nutrient-rich fertilizer.

2. Materials and methods

2.1 Materials

2.1.1 Plant Material

The plant material used for the production of biochar and activated carbon in this study consists of cocoa pod husk waste collected from a local farmer in Oumé, located in the Goh region of Côte d'Ivoire. Cocoa pod husks, which are the outer shells of cocoa fruits, are an abundant by-product of the cocoa industry after bean extraction. These agricultural residues are often considered waste, but they possess valuable properties for the production of biochar and activated carbon due to their high carbon content and organic matter.

The husks were carefully collected from the field. This plant material is critical to the study because of its potential to be converted into biochar and activated carbon (Photo 2).



Photo 2: Dried cocoa pod husks

2.1.2 Glassware and Miscellaneous Equipment

Various equipment and materials were utilized for this study:

Volumetric glassware: Included volumetric flasks, Erlenmeyer flasks, pipettes, graduated cylinders of various capacities, and a graduated burette with its stand for volume measurements.

- Magnetic stirrer: Equipped with a magnetic bar, used for mixing solutions (Photo 3).
- Mortar and pestle: Utilized for grinding the samples (Photo 4).
- Electronic balances: Used for weighing materials and copper samples with precision (Photo 5).
- Sieve: The crushed cocoa pod precursor was sieved using an 8 mm pore sieve (Photo 6).
- pH meter: Employed to measure the pH of solutions (Photo 7).
- Drying oven: Used to dry the cocoa pod husks and activated carbon for 24 hours (Photo 8).
- Electric furnace: Carried out the carbonization of cocoa pod husks (Photo 9).
- Portable biogas analyzer: Used to measure H_2S concentration and detect the presence of this gas (Photo 10).

These tools and equipment were essential for conducting the various stages of the study, from material preparation and analysis to the evaluation of biogas purification.

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Photo 3: Magnetic stirrer



Photo 4: Mortar and pestle



Photo 5: Electronic balances



Photo 6: Sieve



Photo 7: pH meter



Photo 8: Drying oven

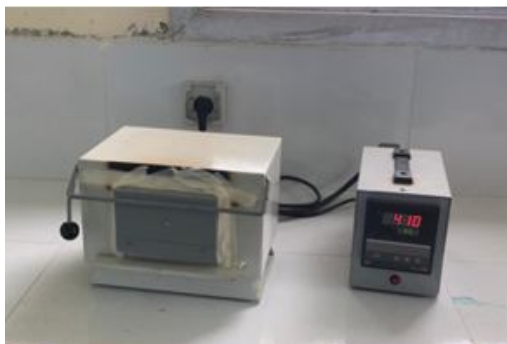


Photo 9: Electric furnace



Photo 10: Portable biogas analyzer

2.2 Methods

2.2.1 Preparation of biochar (Bc)

Samples of leftover cocoapodhusk were pulverized into particles ranging in diameter from 4 to 8 mm. After drying, the ground material was carbonized for 4 hours at a temperature of 450°C in a furnace under an inert atmosphere. After carbonization, the biochar was left to cool in the furnace, still under an inert atmosphere, to prevent oxidation. Cooling was carried out slowly until ambient temperature was reached [22].

2.2.2 Preparation of activated carbon (Ca)

The chemical activation of the ground material was performed using a 500 ppm potassium hydroxide (KOH) solution dissolved in distilled water. The ground material was impregnated with this solution at a concentration of 0.3 g/mL. In hermetically sealed containers, the impregnation process was carried out for six hours at room temperature with frequent stirring to guarantee the mixture was as homogenized as possible.

Following impregnation, the samples were heated progressively in a furnace to prevent thermal shocks and guarantee that the organic components broke down under regulated settings in compliance with carbonization standards [23, 24]. The temperature was increased at a rate of 10°C per minute until it reached 450°C. Once this temperature was achieved, it was

maintained for 4 hours to ensure complete carbonization of the samples. Cooling was carried out slowly until ambient temperature was reached.

The activated carbon was then washed multiple times with distilled water to remove residual KOH and other impurities. Finally, it was dried at a low temperature to obtain a dry product [23, 24].

2.2.3 Characterization of biochar and activated carbon

2.2.3.1 Yield (R)

The yield represents the ratio between the quantity of precursor used and the quantity of filter material obtained after the carbonization process. This measurement is crucial for evaluating the efficiency of the precursor-to-activated-carbon conversion process.

To determine the yield, an initial mass (m_0) of the precursor is measured and subjected to carbonization. After carbonization, the mass (m_1) of the activated carbon produced is measured. The yield percentage is calculated using Equation 1 [25]:

$$R(\%) = \frac{m_1}{m_0} \times 100 \quad (1)$$

2.2.3.2 Ash content

The ash content represents the amount of mineral residues remaining after the combustion of a filter material sample. A high ash content is undesirable as it reduces the quality and adsorption capacity of activated carbon by increasing impurities such as silica, aluminum, iron, magnesium, and calcium.

To determine the ash content, a 0.5 g sample of activated carbon is placed in a crucible and dried in an oven at 80°C for 24 hours. Subsequently, the sample is heated to 650°C for 3 hours. After cooling, the crucible and its contents are weighed again. The ash content (AC) is calculated by comparing the weights before and after combustion [25]:

$$TC(\%) = \frac{m_3 - m_2}{m_1} \times 100 \quad (2)$$

Where:

m_1 : Mass of the activated carbon sample

m_2 : Mass of the crucible and carbon after removal from the furnace

m_3 : Mass of the crucible and carbon after drying

2.2.3.3 Iodine number

The iodine number measures the filter material's capacity to adsorb small molecules in solution, which is crucial for evaluating its microporosity. The method used is detailed as follows:

To determine the iodine number, 0.05 g of the filter material is placed in a beaker containing 15 ml of 0.1N iodine solution and stirred for 4 to 5 minutes. The mixture is then filtered, and 10 ml of the filtrate is transferred into an Erlenmeyer flask. A sodium thiosulfate solution is added until complete decolorization occurs. The volume of sodium thiosulfate used is recorded as V_b , and the iodine number (Id) is calculated using Equation 3 [25]:

$$Id = \frac{(V_b - V_s) \times N \times 126.9 \times \frac{10}{15}}{m} \quad (3)$$

V_b : Volume of 0.1N sodium thiosulfate used for the blank test

V_s : Volume of 0.1N sodium thiosulfate used for the test with the adsorbent

N : Normality of the sodium thiosulfate solution

m : Mass of the adsorbent (0.05 g)

The iodine number provides insight into the adsorbent's efficiency, particularly its microporous surface area, which is critical for applications requiring adsorption of small molecules.

2.2.3.4 Moisture content

The moisture content is determined by measuring the water loss after drying a sample. Five grams of the filter material (m_1) are placed in a crucible, and the combined weight of the

crucible and the material is recorded (m_3). The sample is then dried at 110°C for 2 hours to remove water content. After drying, the crucible and its contents are weighed again (m_2). The moisture content $H(\%)$ is calculated using Equation 4 [25]:

$$H(\%) = \frac{m_3 - m_2}{m_1} \times 100 \quad (4)$$

m_1 : Initial mass of the solid sample (g)

m_2 : Mass of the crucible and the dried activated carbon (g)

m_3 : Mass of the crucible and the activated carbon before drying (g)

This parameter is crucial for assessing the storage stability and adsorption efficiency of the filter material, as high moisture content can reduce adsorption capacity.

2.2.4 Study of copper corrosion rate using the gravimetric method in unfiltered biogas

The purpose of this experiment is to determine how quickly copper corrodes when exposed to unfiltered biogas. The copper samples are cleaned, weighed, and prepared (Photo 11). The samples are placed inside a hermetically sealed bicycle inner tube chamber (Photo 12) connected to a biogas source. The chamber is pressurized to 1 bar with biogas. The copper samples are exposed for specific durations of 168 hours, 336 hours, 504 hours, and 720 hours. Each copper sample has an exposed surface area (A) averaging 0.4635 cm². After the exposure period, the samples are removed, cleaned to eliminate corrosion products, and reweighed to calculate the mass loss (ΔW). The corrosion rate (v) is determined using Equation 5 [25]:

$$v = \frac{\Delta W}{A \times t} \quad (5)$$

Où :

- v Corrosion rate in g.cm⁻² h⁻¹
- ΔW : Mass loss in g.
- A : Exposed surface area in cm².
- t : Exposure time in h.

This methodology aids in evaluating the effect of biogas contaminants on material degradation by offering a quantitative measure of copper corrosion under the influence of unfiltered biogas.



Photo 11: Copper samples



Photo 12: Bicycle inner tube filled with biogas containing copper samples

2.2.5 Biogas filtration

To filter the biogas, 5 g of the filtering material were weighed with a precision of ± 0.01 g and placed into a cylindrical PVC filtration column measuring 10 cm in height and 1.6 cm in diameter. The column was equipped with two stop valves (Figure 1). An acrylic float flowmeter with an accuracy of $\pm 4\%$ was used to regulate the gas flow rate at the column's inlet. The biogas was passed through the adsorbent for a specified contact time. Following this time frame, a biogas analyzer was used to determine the equilibrium concentration of H_2S in the biogas departing the column. This process aimed to evaluate the efficacy of the filtering material in reducing H_2S levels, a key step in improving the quality and usability of biogas.

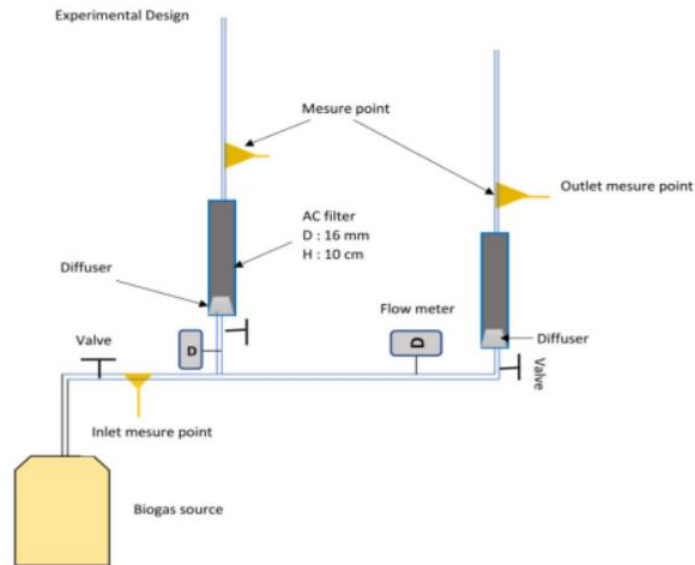


Figure 1: Experimental setup for biogas filtration

2.2.6 Study of copper corrosion rate using the gravimetric method in filtered biogas with a three-factor factorial design

This experiment aims to evaluate the corrosion rate of copper after biogas filtration through two types of filters: biochar (Bc) and activated carbon (Ca). A three-factor factorial experimental design was used to analyze the influence of various factors on copper corrosion.

- Factors studied

Factor A: Type of filter

Two types of filters, biochar (Bc) and activated carbon (Ca), were used to reduce the concentration of H_2S in the biogas. This factor enables the comparison of the efficacy of both filters in mitigating copper corrosion.

Factor B: Pressure

Pressure levels (1 bar and 2 bars) were studied, as pressure may influence the solubility of gases in biogas and subsequently affect the copper corrosion rate.

Factor C: Mass of filter material

The mass of the filter material was considered, as it may impact the H₂S concentration in the biogas after filtration and, therefore, the copper corrosion rate.

- Experimental procedure

Initial weighing: each copper sample was weighed to obtain its initial mass.

Filtration: biogas was filtered through biochar (Bc) or activated carbon (Ca) at pressures of 1 bar or 2 bars, with varying masses of filter material.

Exposure: the filtered biogas was introduced into a hermetically sealed bicycle inner tube, serving as the reaction chamber. Copper samples were exposed to these conditions for 30 days (720 hours).

Post-exposure weighing: after the exposure period, the copper samples were carefully cleaned to remove surface residues and reweighed to determine their final mass.

Corrosion rate calculation: the corrosion rate (ν) was calculated using Equation 5.

- Experimental design

The experiments were conducted following the experimental domain, matrix, and factorial design summarized in Tables 1 to 3. This approach ensured that the interactions between the type of filter, pressure, and filter mass were systematically evaluated to identify their combined and individual effects on copper corrosion. This factorial design provides a robust framework for understanding the efficacy of biochar and activated carbon as filters in mitigating biogas-induced copper corrosion.

Experimental design overview

Table 1: Experimental Domain

Factor	Level -1	Level +1
Type of filter (A)	Activatedcarbon (Ca)	Biochar (Bc)

Pressure (B)	1 bar	2 bars
Mass of filter (C)	5 g	7 g

Table 2: Experiment Matrix

Experiment	Type of filter (A)	Pressure (B)	Mass of filter (C)
1	-1	-1	-1
2	+1	-1	-1
3	-1	+1	-1
4	+1	+1	-1
5	-1	-1	+1
6	+1	-1	+1
7	-1	+1	+1
8	+1	+1	+1

Table 3: Experimental Plan

Experiment	Type of filter (A)	Pressure (B)	Mass of filter (C)
1	Activatedcarbon	1 bar	5 g
2	Biochar	1 bar	5 g
3	Activatedcarbon	2 bars	5 g
4	Biochar	2 bars	5 g
5	Activatedcarbon	1 bar	7 g
6	Biochar	1 bar	7 g
7	Activatedcarbon	2 bars	7 g
8	Biochar	2 bars	7 g

By systematically examining the impacts of each component and how they combine to affect copper corrosion rates, this factorial design offers important new information about how well biochar and activated carbon work to lessen corrosion caused by biogas.

From the multiple linear regression results, the mathematical model describing yield (Y) as a function of the studied factors (Filter Type A, Pressure B, and Filter Mass C) and their significant interactions is expressed as follows:

$$Y = \beta_0 + \beta_A A + \beta_B B + \beta_C C + \beta_{AB} AB + \beta_{AC} AC + \beta_{BC} BC + \beta_{ABC} ABC + \epsilon \quad (6)$$

- Y : Yield.
- A, B, C :Factors.
- β_0 : Averageeffect (intercept).
- $\beta_A, \beta_B, \beta_C$: Coefficients of the main factors.
- $\beta_{AB}, \beta_{AC}, \beta_{BC}, \beta_{ABC}$: Coefficients of significant interactions.
- ϵ : Residualerror.

Standard Deviation Estimation of Coefficients (S_e)

The standard deviation of a coefficient β_i (S_e) is estimated using the following formula:

$$S_e = S/\sqrt{8} \quad (7)$$

S : Estimate of the experimental error variation.

$\sqrt{8}$: Square root of the number of experimental runs.

Estimation of experimental error(S)

The estimation of S is calculated as:

$$s = 8 \times \frac{\sum \beta_i}{n} \quad (8)$$

Where:

β_i : Neglected coefficients.

n : Number of neglected coefficients.

- The model incorporates main effects and interaction terms to account for the complex relationships between the factors.
- The estimation of (S_e) helps quantify the variability in the regression coefficients, ensuring a robust interpretation of the model.
- Neglecting insignificant coefficients reduces overfitting, allowing for a simplified yet accurate representation of the data.

This approach provides a comprehensive understanding of the factors influencing the yield and their interactions, enabling optimization of the biogas filtration process.

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3. Results and discussion

3.1 Characterization of the carbons

3.1.1 Yield

The masses and yields of biochar and activated carbon made from cocoa pod husk waste are summarised in Tables 4 and 5, respectively. The results indicate that the yield of biochar (28.57%) is slightly higher than that of activated carbon (25.75%), despite both being produced at the same temperature of 450°C. This difference in yield, despite the identical temperature, can be attributed to the specific production processes of biochar and activated carbon:

- Carbonization at 450°C decomposes the organic matter in cocoa pod husks, converting a significant portion of the biomass into biochar. This process retains a larger proportion of the initial organic material, leading to a relatively higher yield [26, 27].
- The production of activated carbon involves an additional impregnation phase prior to carbonization. This chemical treatment aims to create pores in the activated carbon to enhance its adsorptive properties [28]. However, this step results in additional material loss. The desired porous structure and enhanced adsorptive capacity in activated carbon require more complex structural modifications, which reduce the overall yield compared to biochar [29].

The observed results are consistent with existing literature. Previous studies on cocoa pod husk waste have similarly shown higher yields for biochar compared to activated carbon:

Comparable biochar outputs to those found in this work were reported by Qayyum et al. (2012), pointing out the fact that simple carbonisation is typically more successful in preserving organic matter [30].

Villamil et al. (2020) found lower yields for activated carbon due to material loss during the activation process, which aligns with our findings [31].

Table 4: Biochar yields

Trial	Initial mass (g)	Biochar mass (g)	Yield (%)
Trial 1	20	5.64	28.20
Trial 2	20	5.76	28.80
Trial 3	20	5.74	28.70
Average	20	5.71	28.57

Table 5: Activated carbon yields

Trial	Initial mass (g)	Final mass of activated carbon(g)	Yield (%)
Trial 1	20	5.20	26.00
Trial 2	20	5.10	25.50
Trial 3	20	5.15	25.75
Average	20	5.15	25.75

3.1.2 Ash content

Tables 6 and 7 present the masses after combustion and the ash content for biochar and activated carbon, respectively, produced from cocoa pod husk waste.

The results indicate that the ash content of biochar is slightly higher than that of activated carbon:

- biochar: Ash content ranges from 6.4% to 7.4%, with an average of 6.8%.
- activated carbon: Ash content ranges from 6.0% to 6.4%, with an average of 6.2%.

The observed differences are attributed to the production processes:

Biochar retains more residual minerals from the original biomass, which leads to a slightly higher ash content.

Activated Carbon, due to its additional chemical activation process, is more effective at reducing residual minerals and impurities, resulting in lower ash content [32]. The results suggest that while the ash content of biochar is marginally higher, it remains within an acceptable range for certain applications [33].

Table 6: Ash content of biochar (Bc)

Trial	Initial mass (g)	Final mass after combustion (g)	Ash content (%)
Trial 1	0.5	0.033	6.6
Trial 2	0.5	0.032	6.4
Trial 3	0.5	0.037	7.4
Average	0.5	0.034	6.8

Table 7: Ash content of activated carbon (Ca)

Trial	Initial mass (g)	Final mass after combustion (g)	Ash content (%)
Trial 1	0.5	0.031	6.2
Trial 2	0.5	0.032	6.4
Trial 3	0.5	0.030	6.0
Average	0.5	0.031	6.2

3.1.3 Iodine number

Tables 8 and 9 summarize the iodine number results for biochar (Bc) and activated carbon (Ca) produced from cocoa pod husk waste.

- activated carbon (Ca): Iodine numbers range between 1050 mg/g and 1150 mg/g, with an average of 1100 mg/g.
- biochar (Bc): Iodine numbers are significantly lower, ranging between 280 mg/g and 300 mg/g, with an average of 290 mg/g.

The substantial difference in iodine numbers between activated carbon and biochar reflects their distinct preparation methods:

- The chemical activation process with potassium hydroxide (KOH), followed by carbonization at 450°C, enhances the material's microporosity.
- Increased microporosity improves the material's adsorption capacity, resulting in a higher iodine number [32].
- Biochar undergoes carbonization without chemical activation, limiting micropore development and reducing its adsorption capacity.
- This results in a significantly lower iodine number [34].

The observed values align with general trends reported in previous studies:

- Activated carbons derived from cocoa pod husks typically exhibit high iodine numbers due to their enhanced microporosity [35].

- Biochar prepared without chemical activation consistently shows lower iodine numbers, highlighting the importance of activation in increasing adsorption capacity [36].

Chemical activation introduces additional pores into the carbon structure, increasing its specific surface area and its ability to adsorb small molecules, such as iodine [32]. Conversely, the simpler carbonization process of biochar results in fewer developed pores, limiting its adsorption performance.

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Table 8: Iodine number of biochar (Bc)

Trial	Iodine number (Id, mg/g)
Trial 1	300
Trial 2	280
Trial 3	290
Average	290

Table 9: Iodine number of activated carbon (Ca)

Trial	Iodine number (Id, mg/g)
Trial 1	1100
Trial 2	1050
Trial 3	1150
Average	1100

3.1.4 Moisture content

Tables 10 and 11 summarize the moisture content results for biochar (Bc) and activated carbon (Ca) produced from cocoa pod husk waste.

- activated carbon (Ca):Moisture content ranges from 8.01% to 8.21%, with an average of 8.13%.
- biochar (Bc):Moisture content is higher, ranging from 13.92% to 14.82%, with an average of 14.25%.

The differences in moisture content can be explained by the production processes:

- activated carbon: the chemical activation process and controlled carbonization reduce the residual water content. The lower moisture content is typical for activated carbon, enhancing its efficiency in applications where minimal moisture is desirable, such as adsorption [79].
- biochar: biochar, produced solely through carbonization, retains more residual moisture due to its less developed pore structure, which tends to trap more water [37]. The higher moisture content may limit its performance in applications requiring high adsorption efficiency or dry conditions.

Table 10: Moisturecontent of biochar (Bc)

Trial	Moisturecontent (H, %)
Trial 1	14.00
Trial 2	14.82
Trial 3	13.92
Average	14.25

Table 11: Moisturecontent of activatedcarbon(Ca)

Trial	Moisture content (H, %)
Trial 1	8.00
Trial 2	8.17
Trial 3	8.21
Average	8.13

3.2. Copper corrosion rate in biogas before filtration

The corrosion rate of copper was measured over different exposure periods to biogas with an H₂S concentration of 100 ppm. Mass losses were observed after 168, 336, 504, and 720 hours, corresponding to mass losses of 0.08 g, 0.13 g, 0.15 g, and 0.19 g, respectively. These mass losses were used to calculate the corrosion rate at each stage. Figure 2 presents the calculated corrosion rates of copper exposed to unfiltered biogas over time. Analysis of the figure shows that the corrosion rate of copper exposed to biogas containing 100 ppm of H₂S progressively decreases as the exposure time increases.

The first notable observation in this study is the relatively high corrosion rate at the beginning of the exposure (168 hours), where a rate of 0.00102738 g.cm⁻².h⁻¹ was measured. This value suggests that copper is immediately attacked by the H₂S present in the biogas. Hydrogen sulfide is well known for its ability to corrode metals, particularly copper, by forming copper sulfide on the surface [38; 39]. This initial reaction is likely the most aggressive, as the copper surface is still clean and fully exposed to the corrosive gas.

As the exposure time increases, a decrease in the corrosion rate is observed. At 336 hours, the corrosion rate decreases to 0.000834746 g.cm⁻².h⁻¹, then to 0.000642112 g.cm⁻².h⁻¹ at 504 hours, and finally to 0.00056934 g.cm⁻².h⁻¹ after 720 hours of exposure. This decrease

suggests that the copper undergoes a form of passivation [40; 41]. The formation of copper sulfide on the metal surface can create a protective layer that slows the progression of corrosion.

This behavior is typical of metals exposed to environments containing specific corrosive agents like H_2S . The progressive reduction in corrosion rate could also indicate that this protective layer becomes increasingly thick and dense, further limiting the access of H_2S to the metal surface [42].

To fully understand the significance of these results, it is essential to compare them with other studies on copper corrosion in similar environments. In the literature, several researchers have studied copper corrosion in the presence of H_2S , and the observed trends are often similar. For example, studies conducted under conditions with comparable H_2S concentrations have shown that the corrosion rate is initially high but decreases over time due to the formation of passivating corrosion products.

However, reported corrosion rates can vary depending on several factors, such as H_2S concentration, temperature, humidity, and even the purity of the copper used in the experiments [43]. *Similar early corrosion rates but a less noticeable decrease over time were observed in a study by Smith et al. (2018) on copper corrosion in a biogas environment. This could be because of a greater H_2S concentration or differing test temperatures. According to their investigation, spectroscopic examination verified the creation of copper sulphide, confirming the theory that the formation of a protective layer is what lowers the rate of corrosion [44].*

Other researchers have found that the corrosion rate may increase again after a certain period if the corrosion product layer becomes too thick and cracks, exposing the underlying metal. This phenomenon was not observed in the present study, possibly due to the shorter exposure.

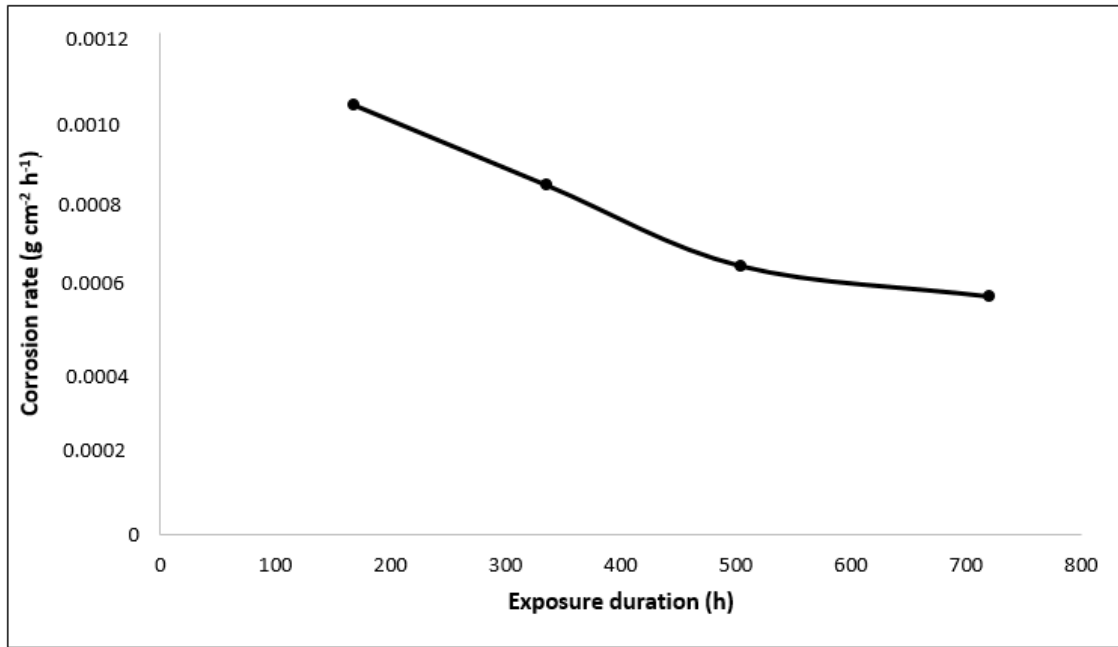


Figure 2: Copper corrosion rate over different periods of exposure to biogas

3.3. Study of copper mass loss (ΔW) in biogas after filtration

This section focuses on evaluating the influence of three critical factors: the type of filter, pressure, and filter mass, as well as analyzing their interactions to determine their impact on the response variable, copper mass loss (ΔW). The experimental results show that copper mass loss ranges from 0.028 g to 0.039 g, depending on the combinations of the factors studied (Table 12). These data emphasize the importance of these variables in the filtration process, particularly in optimizing conditions to minimize copper corrosion in biogas treatment systems.

Table 12: Effect of factors on copper mass loss (ΔW) in biogas after filtration

Experiment	Filter type (A)	Pressure (B)	Mass (C)	ΔW (g)
1	Activatedcarbon	1	5	0.032
2	Biochar	1	5	0.038
3	Activatedcarbon	2	5	0.033
4	Biochar	2	5	0.039
5	Activatedcarbon	1	7	0.028
6	Biochar	1	7	0.034
7	Activatedcarbon	2	7	0.029

8	Biochar	2	7	0.035
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3.3.1. Determination of the mathematical model coefficients for mass loss (ΔW) :examination of the influence of factors

Table 13 and Figure 3 illustrate the effects of these various factors on copper mass loss after biogas filtration through different adsorbents. These coefficients quantify the relative impact of each variable on the corrosion process. A coefficient is considered significant when its absolute value is greater than or equal to twice the standard error (2Se), which corresponds, in this case, to a threshold of 0.0006. Significance indicates that the factor has a statistically relevant influence on mass loss. The coefficient β_0 represents the average ΔW with a value of 0.0335. Thus, the baseline value of ΔW is significant, as expected, since it represents the overall mean without the influence of the factors.

The factor A (Filter type) has a highly significant positive effect on ΔW . Specifically, when the filter type changes from -1 to +1 (i.e., from activated carbon to biochar), ΔW increases on average by 2×0.0030 g. This indicates that biochar, as a filter, significantly increases mass loss compared to activated carbon. Factor A accounts for 54.55% of the total effect on mass loss (Figure 3). In contrast, Factor B (Pressure) does not have a significant effect on ΔW . An increase in pressure by 1 bar leads to only a slight average increase of 2×0.0005 g in ΔW .

Factor B contributes a negligible 9.09% to the total effect (Figure 3). Hence, pressure does not play a major role in copper mass loss in filtered biogas, and its effect can be considered minor.

Factor C (Filter mass), on the other hand, has a highly significant negative effect on ΔW . When C changes from -1 to +1, the mass loss decreases by 2×0.0020 g on average. This factor accounts for 36.36% of the total effect (Figure 3). Therefore, filter mass (C) is also an important factor that significantly influences copper mass loss.

However, all interactions between factors are negligible. They should not be considered as they have no synergistic effect on copper mass loss in filtered biogas.

Based on the significance of the coefficients, the simplified model equation is:

$$Y = 0,0335 + 0,0030 A - 0,0020 C \quad (9)$$

This simplified equation only includes terms that have a significant effect on copper mass loss in filtered biogas. These results highlight that Factors A (Filter Type) and C (Filter Mass) are the primary significant contributors to copper mass loss in filtered biogas.

Table 13: Coefficients of the mathematical model for copper mass loss (ΔW)

Coefficient	Value	Significant
β_0	0.0335	Yes
β_A	0.0030	Yes
β_B	0.0005	No
β_C	-0.0020	Yes
β_{AB}	0.0000	No
β_{AC}	0.0000	No
β_{BC}	0.0000	No
β_{ABC}	0.0000	No

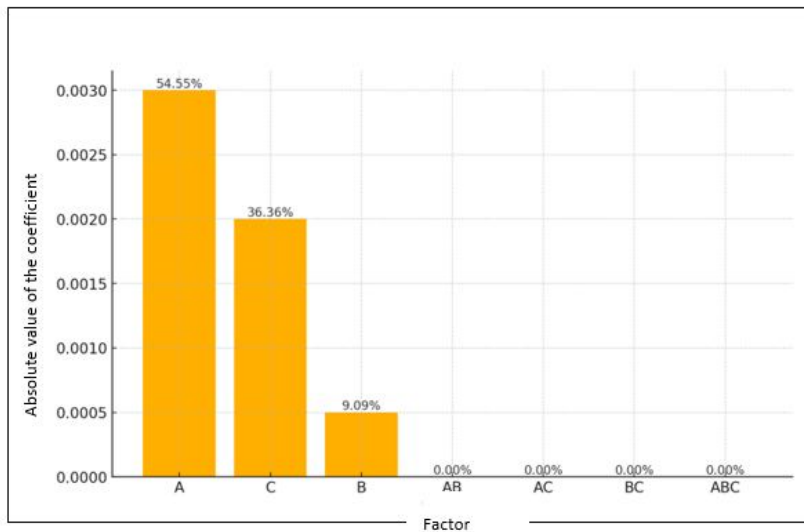


Figure 3: Pareto chart of factors affecting copper mass loss

3.3.2. Coefficient of determination R^2

The coefficient of determination R^2 for the simplified model is 0.97, indicating that the model is highly effective at predicting mass loss based on the given factors. To minimize copper mass loss, it would be preferable to use activated carbon as the filter material with a high mass, while making minor pressure adjustments depending on operational constraints.

3.4. Study of copper corrosion rate in biogas after filtration: examination of the influence of factors

This section concentrates on the unique effects of factors A, B, and C as well as how they interact with one another to affect the response variable, copper corrosion rate (Δv) (Table 14). This analysis provides insight into how each factor influences copper corrosion and offers valuable guidance for optimizing filtration conditions, thereby mitigating the detrimental effects of corrosion.

Table 14: Effect of factors on copper corrosion rate in biogas after filtration

Experiment	Filter type (A)	Pressure (B)	Mass (C)	Δv ($\text{g} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$)
1	Activated carbon	1	5	9.59×10^{-5}
2	Biochar	1	5	1.14×10^{-4}
3	Activated carbon	2	5	9.89×10^{-5}
4	Biochar	2	5	1.17×10^{-4}
5	Activated carbon	1	7	8.39×10^{-5}
6	Biochar	1	7	1.02×10^{-4}
7	Activated carbon	2	7	8.69×10^{-5}
8	Biochar	2	7	1.05×10^{-4}

3.4.1. Determination of mathematical model coefficients for corrosion rate

Table 15 and Figure 4 provide a clear representation of the effects of these factors on copper mass loss after biogas filtration through different adsorbents. These results highlight the influence of each factor and their interactions on copper corrosion rate. The value of $2Se$ is 2.00×10^{-6} , indicating that the coefficients β_0 , β_A and β_C are significant.

Factor (A) has a significant effect on the corrosion rate. When it transitions from the low level (-1), corresponding to activated carbon, to the high level (+1), biochar, the corrosion rate increases on average by 1.80×10^{-5} g, highlighting the importance of filter selection. This factor accounts for 56.07% of the total effect on the copper corrosion rate (Figure 4).

Although biochar has a high specific surface area and some adsorption capacity, it can allow corrosive compounds such as H_2S and residual moisture to pass through or even generate them, which are not entirely neutralized. These chemical differences influence the interaction of residual molecules with copper, thereby increasing the corrosion rate. In contrast, activated carbon, due to its porous structure, is more effective at capturing a variety of contaminants, reducing their potential to cause corrosion [46].

Transitioning Factor B (Pressure) from the low to the high level increases the corrosion rate by an average of 3.00×10^{-6} g. Compared to A, Factor B has a more moderate but still positive effect on the corrosion rate. This factor represents 6.54% of the total effect on copper corrosion rate (Figure 4).

This increase, although less pronounced than that caused by the filter type (Factor A), shows that pressure plays an essential role in the corrosion process, albeit with less direct impact. Pressure mainly influences the physical aspects of the corrosion process, such as gas density and diffusion, as well as the frequency and energy of collisions between gas molecules and the metal surface. At higher pressures, the concentration of corrosive gas (H_2S) in contact with the metal increases, which may accelerate the electrochemical reactions responsible for corrosion [47].

However, this moderate effect is explained by the fact that pressure does not alter the chemical composition of the gases present in biogas, unlike the filter type, which can introduce or remove certain corrosive agents [47]. In other words, while the filter type directly determines the chemical nature of the corrosive environment, pressure influences how this environment interacts with the metal. This explains why increasing pressure leads to a rise in the corrosion rate but is less pronounced than the change in filter type.

The negative coefficient associated with Factor C (Filter Mass) indicates an inverse effect on the corrosion rate. When the filter mass increases from the low to the high level, the corrosion rate decreases on average by 1.20×10^{-5} g. This significant effect underscores the importance of filter mass in reducing corrosion. Factor C represents 37.38% of the total effect on copper corrosion rate (Figure 4).

Increasing the filter mass enhances the system's ability to adsorb impurities and corrosive agents, such as H_2S , present in biogas, thereby reducing their interaction with metal surfaces. A larger mass of adsorbent offers a more extensive active surface area, improving filtration efficiency and decreasing the concentration of corrosive substances in the filtered gas.

Consequently, increasing the filter mass allows for more effective capture of compounds like H_2S , the primary contributors to corrosion, thereby limiting the wear of metallic equipment [48]. This result demonstrates the advantage of increasing filter mass to minimize corrosion, providing a practical strategy to prolong the lifespan of equipment. This factor should be carefully considered when designing and optimizing biogas filtration systems in industrial applications to ensure maximum protection against corrosion.

The interactions AB, AC, and BC do not have a significant effect on the corrosion rate. This means that the combined effects of these factor pairs do not significantly alter the response beyond the individual effects of the factors. In this experiment, the effects of Factors A, B, and C can be considered independently, as there are no significant interactions between them. The percentages shown in the Pareto chart (Figure 4) indicate that Factors A and C combined account for the majority of the total effect on the corrosion rate. The other factors contribute very little and can be considered negligible in this context.

Based on the significance of the coefficients, the simplified model equation is:

$$Y = 1,00 \cdot 10^{-4} + 9,00 \cdot 10^{-6}A - 6,00 \cdot 10^{-6}C \quad (10)$$

This simplified equation includes only the terms that have a significant impact on the copper corrosion rate in filtered biogas. The results show that Factor A (Filter Type) and Factor C (Filter Mass) are the primary contributors with a notable effect on the copper corrosion rate in this context.

Table 15: Coefficients of the mathematical model for corrosion rate (Δv)

Coefficient	Value	Significant
β_0	1.00×10^{-4}	Yes
β_A	9.00×10^{-6}	Yes
β_B	1.05×10^{-6}	No
β_C	-6.00×10^{-6}	Yes
β_{AB}	0.00	No
β_{AC}	3.39×10^{-21}	No
β_{BC}	0.00	No
β_{ABC}	0.00	No

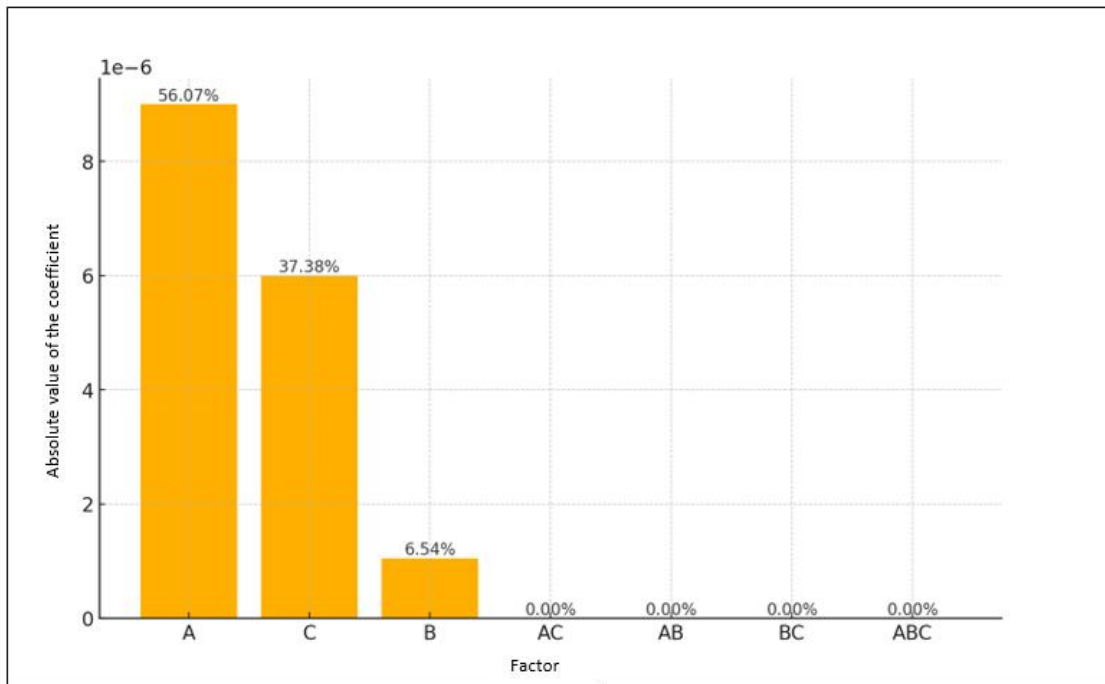


Figure 4: Pareto chart of factors affecting the copper corrosion rate

3.4.2. Coefficient of determination

The coefficient of determination R^2 for the simplified model is 0.91, indicating a strong ability of the model to predict the corrosion rate based on the studied factors. As with mass loss, to minimize the corrosion rate, it is recommended to use activated carbon as the filter material, with a high mass, while making slight pressure adjustments according to operational constraints.

3.5. Comparison of copper corrosion rate in biogas before and after filtration

Figure 5 compares the copper corrosion rate in biogas over 720 hours of exposure, both before and after filtration. The results clearly show that the corrosion rate is significantly reduced after filtration, with higher efficiency observed when activated carbon is used as the filter material compared to biochar. The comparison of copper corrosion rates in biogas before and after filtration reveals significant differences influenced by filtration factors.

Before filtration, copper exposed to biogas containing 100 ppm of H_2S exhibits an initially high corrosion rate, which gradually decreases over time due to the formation of a protective copper sulfide layer. This decrease suggests some level of passivation of the copper, but corrosion remains a persistent issue.

After filtration, the analysis of factor effects shows that the corrosion rate is primarily influenced by Filter Type (Factor A) and Filter Mass (Factor C). Using biochar instead of activated carbon, as well as reducing filter mass, increases the corrosion rate. Conversely, a higher mass of activated carbon decreases the corrosion rate.

The simplified model developed after filtration, with a coefficient of determination $R^2=0.91$, confirms that to minimize corrosion, it is recommended to use activated carbon with a high filter mass. Pressure should be adjusted according to operational constraints.

This comparison exhibits how well filtering works and how crucial it is to choose the right parameters in order to prolong the life of metal equipment exposed to biogas.

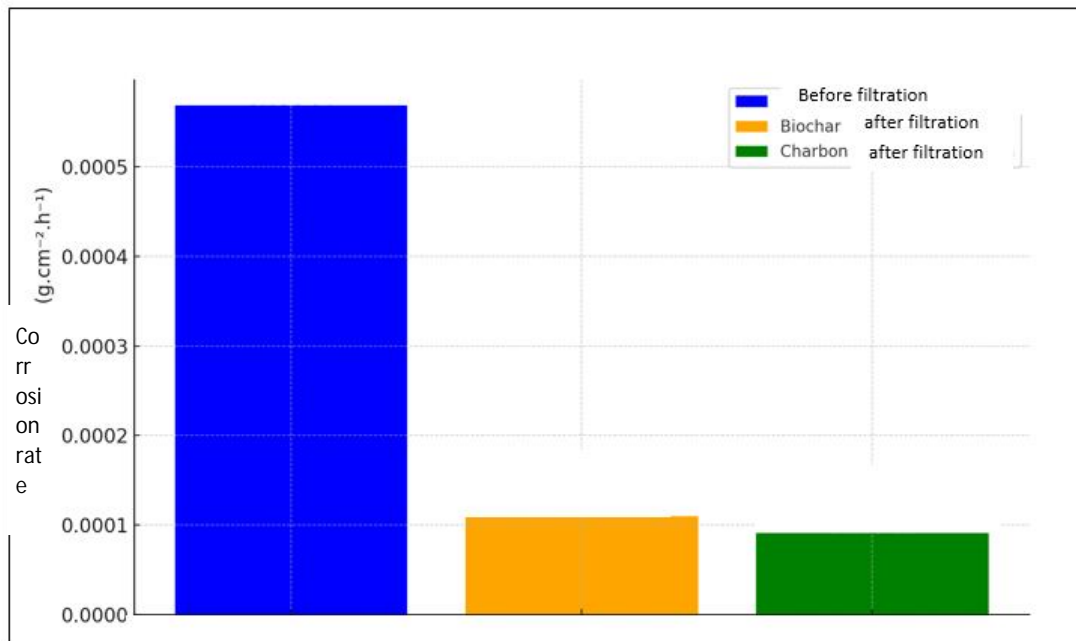


Figure 5: Comparison of copper corrosion rate in biogas before and after filtration

4. Conclusion

This study demonstrated the effectiveness of activated carbon and biochar, derived from cocoa pod waste, in reducing copper corrosion in contact with biogas containing hydrogen sulfide (H_2S). The results showed that activated carbon, due to its microporous structure, significantly reduced the corrosion rate to an average of $8.39 \times 10^{-5} \text{ g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$, representing a reduction of over 40% compared to unfiltered biogas. In comparison, while biochar was less effective with an average rate of $1.02 \times 10^{-4} \text{ g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$, it remains a more

economical and sustainable alternative, particularly suitable in contexts where local resources and environmental considerations are paramount.

The factor analysis highlighted that filter type (activated carbon or biochar) and filter mass play a crucial role in reducing corrosion. Using 7 g of activated carbon resulted in a further 30% reduction in the corrosion rate compared to 5 g. These findings confirm that increasing the filter mass significantly enhances the adsorption efficiency of impurities such as H₂S. The use of carbon materials derived from agricultural waste not only extends the lifespan of metal infrastructure exposed to biogas but also promotes waste valorization while reducing the carbon footprint. As a practical example, these results could be applied in agricultural or industrial biogas systems, where biogas purification is critical to protecting infrastructure and optimizing operational costs. This study could be expanded by exploring combinations of filters or varying experimental conditions (e.g., changes in temperature and exposure duration). Furthermore, a comparative cost analysis of biochar and activated carbon under real-world conditions would provide practical recommendations for large-scale projects.

Disclaimer (Artificial intelligence)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

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