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ORIGINAL RESEARCH ARTICLE

Study of aluminum corrosion in contact with biogas before and after purification on different carbons.

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ABSTRACT

The study of aluminium corrosion in contact with biogas before and after purification on different types of carbon aims to understand the impact of impurities present in biogas, in particular hydrogen sulphide (H_2S), on aluminium degradation. The study highlights the importance of biogas purification in minimising aluminium corrosion. Depending on the level of purification and the types of carbon used for filtering, it is possible to improve the durability of infrastructures in contact with biogas. This has direct implications for the maintenance and operating costs of facilities using biogas as an energy source. Hydrogen sulfide (H_2S) is a colorless, flammable and highly toxic gas characterized by an unpleasant odor. It is often present in industrial and natural environments, particularly in biogas. This gas is involved in the degradation of metals used in anaerobic digestion equipment, in the petrochemical industry, etc. The aim of this work is to study the performance of biochar and activated carbon prepared from corn cobs in removing H_2S from biogas, and to evaluate the reduction of the corrosive effect of filtered biogas on metallic aluminum. The impregnation and carbonization method was used to prepare activated carbon from corn cobs, and the gravimetric method to study the corrosion rate of metal in biogas. The results indicate that the activated carbon prepared is microporous, has a good specific surface and a better adsorption capacity. Furthermore, the prepared activated carbon samples also showed good H_2S removal efficiency in the biogas. The aluminum-induced protective power values in filtered biogas for biochar and activated carbon are 58 % and 82.22 % respectively. We plan to increase the contact time and experiment with other metals and carbons.

Keywords: biogas; aluminium; corrosion; gravimetric method; hydrogen sulfide

1. Introduction

The corrosion of metals in contact with gases containing impurities such as biogas is a well-studied phenomenon because of its impact on the durability of industrial infrastructures and equipment. The literature shows that aluminium, despite its protective properties under mild oxidising conditions, does not resist effectively in the presence of acid and sulphide environments, particularly in systems using untreated biogas[1]. Biogas is a renewable energy source with many environmental benefits[2-5]. It is a gas composed largely of combustible methane (CH4) and carbon dioxide (CO2), but can also contain impurities such as hydrogen sulphide (H_2S), ammonia (NH_3) and volatile organic compounds (VOCs)[6]. Hydrogen sulphide is very dangerous for humans and the environment, particularly because of its toxicity. It is the cause of numerous corrosion problems in many industries such as gas and petrochemicals[7,8]. As a result, it is likely to shorten the life of transport pipelines and processing plants in the oil and gas industries[9,10]. It is therefore necessary to eliminate it from biogas from a technical, environmental and health point of view. Several studies have shown that purifying biogas with activated carbons improves the durability of aluminium systems, particularly sulphide attacks[11,12]. Treating H2S in biogas using local, easily accessible and inexpensive materials would therefore be a major asset for Côte d'Ivoire, which is an agricultural country. Activated carbon adsorption also presents a number of opportunities, as it is less expensive and also offers high efficiency for H2S adsorption [13-15], as well as for pollutant removal thanks to high-performance adsorbents[16-18]. The selection of activated carbon is therefore critical for optimising purification performance and minimising corrosion[19]. A number of scientific studies have examined the use of activated carbon as an adsorbent[20]. In the case of our study, we were interested in maize cobs, which are available and accessible throughout Côte d'Ivoire. The general objective of our work is to study the performance of activated carbon and biochar prepared from maize cobs available in Côte d'Ivoire, with a view to reducing the corrosive effect of H2S in biogas, and to assess the oxidising power of filtered biogas on aluminium. This study provides essential elements for improving the durability of exposed aluminium infrastructure through understanding corrosion mechanisms, assessing purification and optimising filtration systems[21,22].

2. Materials and methods

This section includes study, sampling, laboratory and computer equipment.

2.1. Aluminum metal treatment

For the treatment of aluminum metal, we used scraper paper of different granulometry, acetone and then rinse it thoroughly distilled water. The metals were dried in an oven at 40°C for 5 min Samples are weighed using a precision balance. **Figures 1** and **2** below show the aluminium samples and the study balance.

Figure 1. Aluminum samples.

Figure 2. precision balance.

2.2. Portable biogas analyzer

Detection of H2S concentration with the help of a portable biogas detector. It was used to detect the presence of H_2S. It is also a filtered (H_2S-free), portable biogas detector with a 4.5" LCD screen. It can also monitor CO, O_2 and combustible gases simultaneously. The instrument features two instantaneous alarms with audio/visual and vibration indicators, rechargeable battery and simple operation. BOSEAN has a charge time of between 6h and 8h. It weighs 400 g (with battery) and has a gas sensor lifetime of 2 years. To use it, simply press and release the <<On >> button for 3 seconds. After the buzzer it enters the detection state and then emits a brief sound once the detector is switched on. Response time is 30s, LED alert, audio and vibration for gas leak, low fault. At this point, it displays the concentration of O_2, H_2S, CO and CH_4 (the percentage of biogas) and any combustible gas in the environment. **Figure 3** below shows Portable biogas analyzer.

Figure 3. Portable biogas analyzer.

2.3. Hydrogen sulphide (H_2S)

Hydrogen sulphide (H_2S) is a colourless, flammable and toxic gas, recognisable by its characteristic rotten egg smell. It occurs naturally in many environments and can also be produced by various industrial activities.

2.3.1. Characteristics, sources and effects on health and the environment

- Characteristics

Chemical formula: H_2S

Odour: Unpleasant rotten egg odour at low concentrations.

Toxicity: H_2S is extremely toxic and can be fatal in high concentrations. Even at low concentrations, it can cause irritation of the eyes, respiratory tract, and headaches. Flammability : H_2S is flammable and can form explosive mixtures with air.

-Natural Sources:

Decomposition of Organic Matter: H_2S is produced by the anaerobic decomposition (in the absence of oxygen) of sulphur-rich organic matter by bacteria.

Geothermal Sources: H_2S is found in geothermal areas, such as volcanoes, hot springs, and geysers.

Natural Gas and Crude Oil: H_2S is present in some natural gas and crude oil reserves.

-Industrial sources:

Oil and Natural Gas Processing: H_2S is often a by-product of oil refineries and natural gas processing.

Chemical Industry : H_2S is used in the production of various chemicals, including elemental sulphur and metal sulphides.

P-Effects on Health and the Environment

- Human health:

Acute exposure: Exposure to high concentrations can cause loss of consciousness, convulsions and even death. At very low concentrations, it can cause irritation of the eyes, nose and throat.

Chronic Exposure: Repeated or prolonged exposure to low concentrations of H_2S may cause chronic respiratory symptoms, headaches, and fatigue.

Odour and Detection: Although H_2S has a strong odour, prolonged exposure can desensitise the sense of smell, making the gas even more dangerous.

-Environnement :

Corrosion: H_2S is corrosive to many metals, causing problems in industrial plants and biogas treatment infrastructures.

Atmospheric pollution: H_2S contributes to air pollution and can form acid rain when it combines with water in the atmosphere to form sulphuric acid (H_2SO_4).

2.3.2. Management and treatment of hydrogen sulphide

-Desulphurisation:

In the biogas and natural gas industry, H_2S is often removed by desulphurisation processes. This can include adsorption on materials such as activated carbon or iron oxide, or biological processes using bacteria capable of oxidising H_2S to elemental sulphur.

Ventilation and Detection: Risk areas must be well ventilated, and H_2S detectors must be installed to alert in the event of a leak.

Personal Protective Equipment (PPE): Workers exposed to H_2S must wear appropriate protective equipment, such as respirators and protective clothing.

-Industrial uses

Production of Sulphur: H_2S is an important source of sulphur in the chemical industry. Synthese of Chemicals: It is used in the synthesis of various sulphur compounds.

2.4. H_2S elimination test by adsorption on coal (CAEM and BEM) Brin Foundation experimental site

The biogas was used on a poultry farm in the Bondoukou region. The farm has a 20 m^3 methanizer for processing hen droppings (poultry waste). **Figure 4** below shows Overview of Methanize.

Figure 4. Overview of Methanizer.

1: Methanizer; 2: Manual feed tank; 3: Automatic feed tank; 4: Outlet; 5: Methanization digestate tank (liquid & solid fraction);

6: Filtering and purifying system of Biogas;

7: Temperature sensors (digester and digestate).

2.5. Removal efficiency method

Concentration measured in biogas sample at the inlet / outlet of filter using a portable biogas detector.

The flow rate of the biogas was maintained at 0.146 m^3/min (0.00244 m^3/s) during all tests conducted

2.6. Gravimetry

2.6.1. Definition

Method for determining corrosion rate based on mass loss. This is a simple technique and can be described as the immersion of surface samples (S) under study in corrosive media; i.e., upon weighing at regular time intervals, weighed S specimens will become more familiar with these types by dipping into them for defined times [23]. After this the sample is weighed again to measure mass variaty and it show the Δm values.

$\Delta m = m_0 - m_1$ (6)

m_0 : Initial sample mass (g).

m_1: Final sample mass (g).

Δm : the variation in mass (g).

2.6.2. Preparation of the sample:

- The sample containing the analyte (the substance to be analysed) is prepared so that it is in a homogeneous form and the analyte is in a known chemical form.

Precipitation:

- A reagent is added to the sample to form an insoluble precipitate with the analyte.

Filtration:

- The precipitate is then separated from the rest of the solution by filtration. It is crucial that filtration is carried out correctly to avoid loss of the analyte.

Washing :

- The precipitate is washed with distilled water or a suitable solvent to remove impurities adsorbed to its surface. The wash must be sufficiently effective to ensure the purity of the precipitate, but without causing significant dissolution of the precipitate.

Drying or Calcination:

- The washed precipitate is dried at a suitable temperature or calcined (heated to a high temperature) to remove any water or other volatile components. This process produces a final product of known composition.

Weighing:

- The dry precipitate is accurately weighed using an analytical balance. The measured mass is used to calculate the amount of analyte present in the initial sample Determination of metal ions: Ions such as calcium (Ca^{2+}) can be determined by precipitating them as calcium oxalate (CaC_2O_4), followed by calcination to obtain calcium oxide (CaO), which is then weighed.

Advantages of the Gravimetric Method

Accuracy: The method is extremely precise and reliable, as it is based on the measurement of mass, a physical quantity that can be measured with great accuracy.

- Purity: The precipitates used are often of high purity, which contributes to the reliability of the results.

- Simple equipment: The technique does not require sophisticated instruments, just an accurate analytical balance.

2.6.3. Disadvantages of the gravimetric method

Time consumed: The method is often lengthy, involving several stages of filtration, washing and drying.

-Loss of material: There is a risk of losing the analyte during the filtration or washing stages.

- Precipitate specificity: The method requires the analyte to form a specific precipitate with precise properties (insolubility, well-defined stoichiometry).

2.7. Experimental protocol

Gravimetry is an experimental method used to determine the mass of a sample in time, exponsed into corrosive environment.

The above-mentioned method procedure for our case as an experiment is:

- After weighing keep the sample in air chamber containing biogas, m1
- Remove the sample for 5 hours, 24 hours, 48 and at last after every second passage.
- Scrub cleaned with only distilled and deionized water.
- Dry in an oven and reweigh, m2 the new mass

Figure 5 below shows Biogas inner tube and aluminum sample.

Figure 5. Biogas inner tube and aluminum sample.

2.8. Corrosion speed

Corrosion rate value is the average of three test done under same conditions. Experiments were performed using a large number of samples of different masses with each metal being exposed to biogas in an air chamber for 5, 24, or 72 h.

The average weight loss mass of corrodent copper [W] were calculated.

With:

$$W = \frac{\Delta m}{S.t} [mg.cm^{-2} h^{-1}] \quad (7)$$

Δm : mass loss (g) ;

S : total surface area of the sample (cm^2);

t : immersion time (h).

3. Results and discussion

3.1. Study of the efficiency of hydrogen sulphide elimination from biogas by coal (CAEM and BEM)

A methanizer, which generates biogas from methane (CH4), carbon dioxide (CO2), carbon monoxide (CO), and hydrogen sulfide (H2S), is another feature of the plant. There was no change from the initial H2S concentration in variations in the H2S concentration prior to adsorption during operation. This suggests that during the operation period, the starting H2S concentration did not change. **Table 1** below concerns Biogas composition.

Table 1. Biogas composition.

Constituants	Mesure 1	Mesure 2	Mesure 3	Mesure 4
CH_4	85-90 %	85-90 %	85-90 %	85-90 %
CO	10-15 ppm	85-90 ppm	85-90 ppm	85-90 ppm
H_2S	80 – 100 ppm	80 – 100 ppm	80 – 100 ppm	80 – 100 ppm

3.2. Study of metal aluminium corrosion in biogas

3.2.1. Evolution of the corrosion speed as a function of the study time in the case of aluminum in the presence of activated carbon based on corncobs (CAEM) and biochar (BEM)

Figures 6 and **7** show the evolution of corrosion rate as a function of study time in the case of aluminum in the presence of corncob activated carbon (CAEM) and biochar (BEM).

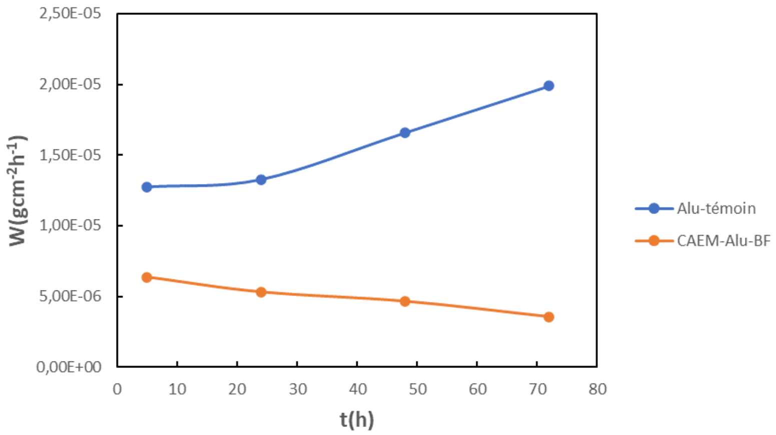

Figure 6. Corrosion rate vs. study time for aluminum in the presence of corncob activated carbon (CAEM).

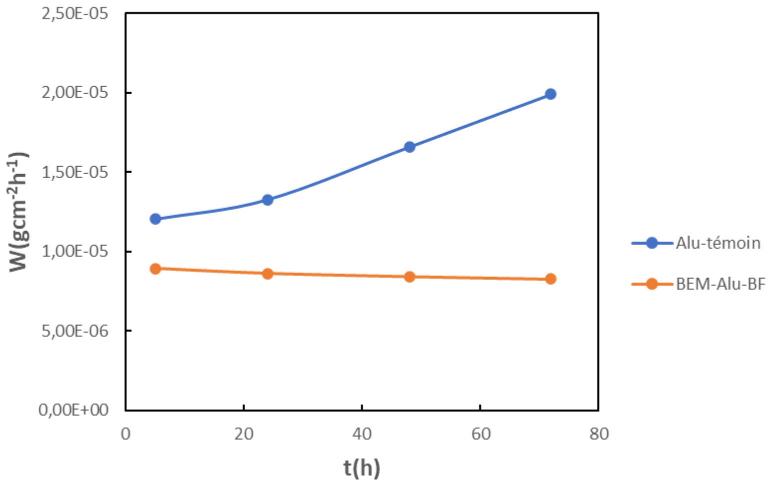

Figure 7. Corrosion rate vs. study time for aluminum in the presence of biochar (BEM).

These figures indicate that, in the case of aluminum (control), in unfiltered biogas (BNF), the corrosion rate increases with research time. A more aggressive corrosion process is indicated by the high corrosion rate, which is characterized by increased mass loss[24, 25]. This could be explained by the constant loss of aluminum (Al) owing to its weakening in its immediate surroundings due to the high concentration of moisture and hydrogen sulfide (H2S). The converse was seen with filtered biogas (BF), i.e., a reduction in corrosion rate. Aluminum exposed to BF experiences a lower rate of corrosion, which is indicative of a low mass loss of the element. The inhibitory effect of the two carbons (BEM and CAEM) is the cause of this minimal mass loss. In actuality, the BF's high H2S and water concentrations, which were causing the corrosion rate to accelerate, were lowered due to the molecules' absorption by the carbon filter. It should be mentioned that the metal's corrosion rate is significantly higher when BEM is present than when CAEM is present[25-27].

3.2.2. Comparative study of the corrosion rate of aluminum as a function of time in filtered biogas (BF) in the presence of different corn cob-based carbons (CAEM and BEM)

Figure 8 shows a comparative study of the corrosion rate of aluminum as a function of time in filtered biogas (BF) in the presence of corncob-based carbons (CAEM and BEM).

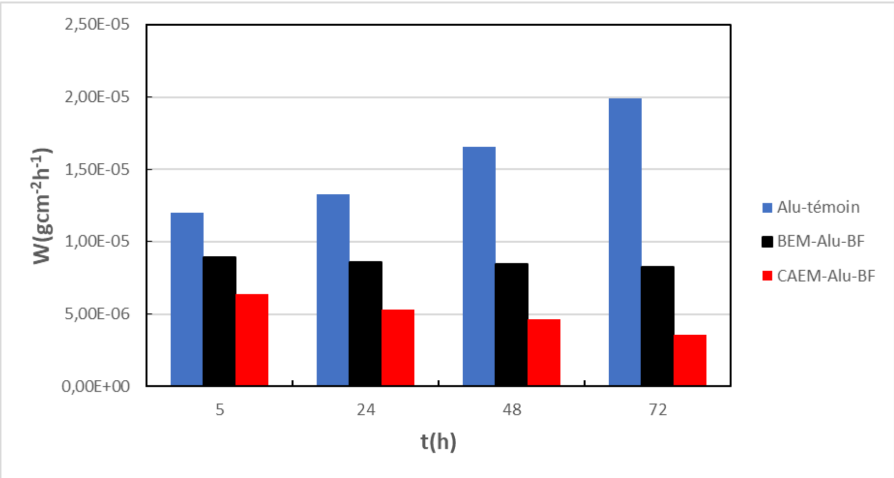

Figure 8. Comparison of aluminum corrosion rates as a function of time in filtered biogas (control) in the presence of corncob activated carbon (CAEM) and biochar (BEM).

Figure 8 shows a comparison of aluminum corrosion rates as a function of time in biogas in the presence of activated corn charcoal and biochar. A decreasing trend in metal corrosion rate is observed in both situations

(CAEM and BEM). This could be explained by the inhibiting effect of the charcoal on aluminum corrosion in contact with the filtered biogas. In addition, CAEM is more effective than BEM.

3.3. Study of induced protective power (PPI)

Induced corrosion protection of metals in biogas environments refers to mechanisms or techniques that reduce or prevent corrosion of metals when exposed to the corrosive environments present in biogas. One example is the control of the biogas environment. For example, limiting the concentrations of H_2S, moisture and other corrosive compounds in the biogas can reduce the rate of corrosion. This can include biogas purification processes. Induced protective power therefore refers to all measures that are taken to create protection around metals in contact with biogas in order to extend their life and avoid breakdowns due to corrosion.

3.3.1. Study of filtration-induced protective power as a function of time in the presence of corncob activated carbon (CAEM)

Figure 9 below shows the evolution of filtration-induced protective power as a function of time in filtered biogas in the presence of corncob activated carbon (CAEM).

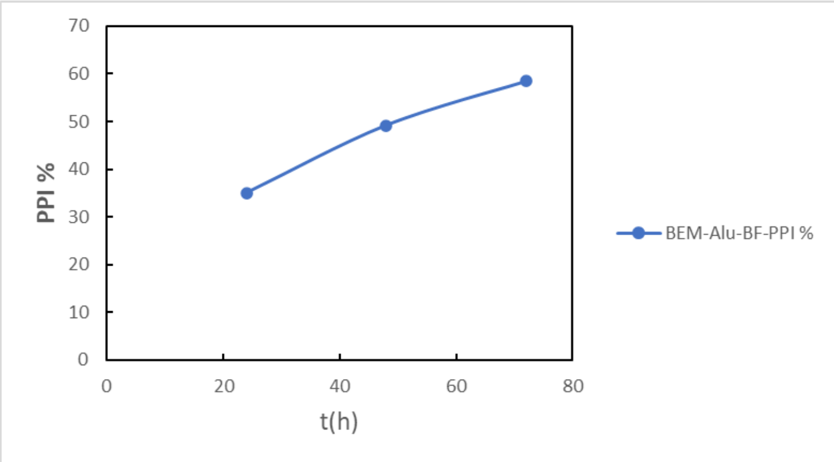

Figure 9. Evolution of filter-induced protective power in filtered biogas (case of aluminum in corncob activated carbon).

This figure's analysis reveals that the induced protective power rises from 50 to 82.22% with time. This would suggest the existence of an ever-expanding physical barrier that covers a significant portion of the metal surface with residues of activated carbon. Our metal would be largely shielded from the harsh environment in this way[25–28]. In filtered biogas, activated carbon derived from corn cobs exhibits good corrosion protection against aluminum.

3.3.2. Study of filtration-induced protective power as a function of time in the presence of corncob biochar (BEM)

The **figure 10** below shows the evolution of filtration-induced corrosion protection as a function of time in filtered biogas in the presence of corncob biochar (BEM).

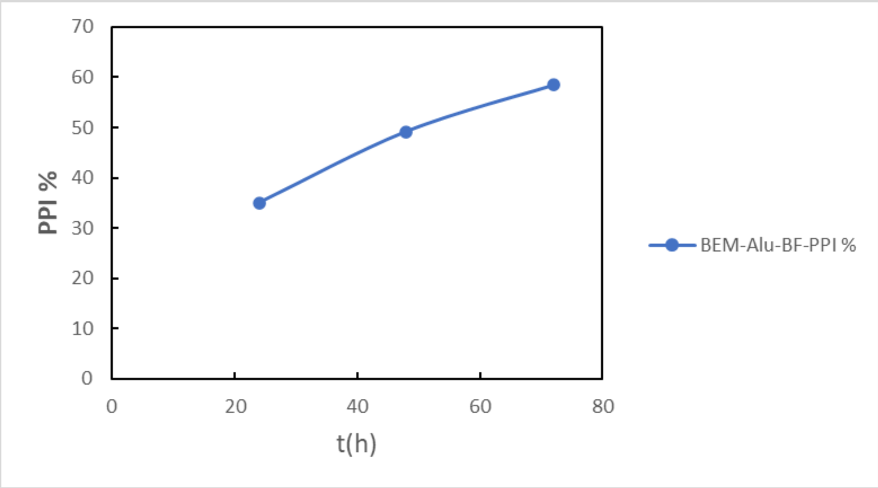

Figure 10. Evolution of induced protective power in filtered biogas (case of aluminum in biochar (BEM)).

This figure's analysis reveals that the protecting power rises from 25.93 to 58.44% with time. This would also point to the existence of a physical barrier that would progressively spread, covering the metal surface with biochar traces at a certain rate. A portion of our metal would be shielded from the harsh surroundings in this way[25–29].

3.4. Comparative study of the induced protective capacity of aluminum as a function of time in filtered biogas (BF) in the presence of corn cob activated carbon (CAEM) and biochar (BEM).

Figure 11 shows a comparison of the induced protective power of aluminum in filtered biogas (BF) in the presence of corncob activated carbon (CAEM) and biochar (BEM).

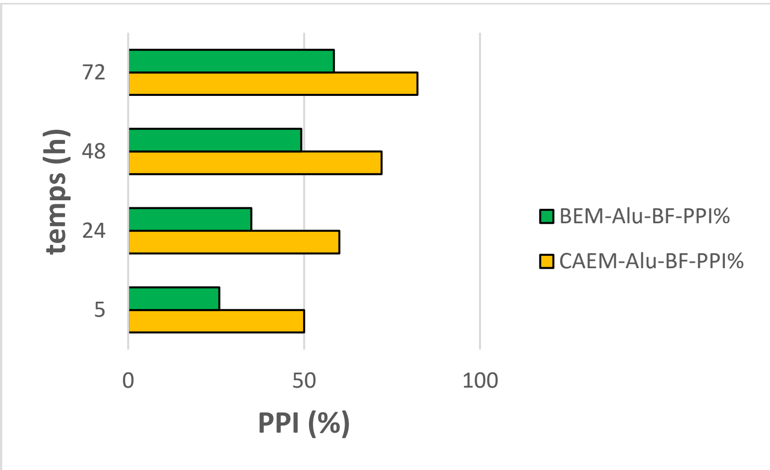

Figure 11. Comparison of aluminum-induced protective capacity in filtered biogas (BF) in the presence of corncob activated carbon (CAEM) and biochar (BEM).

Analysis of this figure shows that for all study times, the induced protective power of aluminum in filtered biogas in the presence of CAEM is greater than that of aluminum in filtered biogas in the presence of BEM. This could be explained by the higher inhibitory power of CAEM. Consequently, aluminum in the presence of CAEM is more resistant to corrosion in filtered biogas than aluminum in the presence of BEM in filtered biogas. CAEM activated carbon has good and better protective properties[30].

4. Conclusion

This study highlighted the corrosive effects of biogas on aluminium, particularly in the presence of impurities such as hydrogen sulphur (H_2S). It has been shown that aluminium, a metal renowned for its resistance to corrosion in conventional oxidising environments, undergoes rapid degradation in a sulphide environment, characteristic of unpurified biogas. The iodine value, yield and ash content of activated carbon made from corn cobs were 647.19 mg/g, 45% and 3.94% respectively. These results show that the activated carbon produced is light, of high quality and microporous (0-2 mm). The high concentration of water molecules and hydrogen sulphide in unfiltered biogas (UBG) is thought to be the cause of the increased corrosion rate that occurs when aluminium comes into contact with it at different times. The protective impact of our carbons, in particular the activated carbon in contact with the biogas, is responsible for the downward trend in the corrosion rate as a function of time in aluminium-filtered biogas (BF). When aluminium is present in biogas filtered with activated carbon and biochar, the induced protective power (also known as the surface coverage rate) is 58.44% and 82.22%, respectively. Activated carbon (CAEM) therefore offers greater protection. In conclusion, biogas purification using activated carbons is an effective strategy for minimising corrosion of metallic materials, such as aluminium, used in biogas treatment plants. This study highlights the importance of optimising filtration processes to improve the durability of equipment and infrastructure in biogas environments.

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Conflict of interest

The authors declare no conflict of interest

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