Nonconventional characterization of cow manure: Electrical Impedance Spectroscopy, and X-Ray diffraction analysis

N.P Arias[1,*], J.J Hoyos-Sebá[1]Jorge Hernández-Ruydiaz[1], J. Salcedo-Mendoza[1], C.A Cardona[2]

[1] Facultad de Ingeniería. Grupo de Investigación PADES, Universidad de Sucre, Sincelejo, Sucre, 700001, Colombia

[2] Instituto de Biotecnología y Agroindustria, Departamento de Ingeniería Química, Universidad Nacional de Colombia sede Manizales, Km 07 vía al Magdalena, Manizales Colombia.

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*Presenting author email: npariasd@gmail.com, nayda.arias@unisucre.edu.co

1. Introduction

Traditionally, cow manure is used for fertilizer (Hamedi et al., 2022) or in biogas production (Herwintono et al., 2020), and more recently as a feedstock for biorefineries (Awasthi et al., 2019; Khoshnevisan et al., 2021). In biogas production, the chemical structure of cow manure is important for the anaerobic digestion processes(Schott et al., 2023) due to the presence of more easily digestible nutrients and organic compounds (Huhtanen et al., 2021). The major nutrients present in manure include phosphorus, nitrogen, potassium, carbon, sulfur, calcium, and magnesium (Huhtanen et al., 2021). The most digestible organic compounds include carbohydrates, lipids, proteins, and fibers. These compounds are broken down into simpler molecules during anaerobic digestion, allowing microorganisms to produce biogas.

On the other hand, pyrolysis (Valizadeh et al., 2022), hydrothermal carbonization (Goldfarb et al., 2022), and hydrothermal liquefaction(dos Passos et al., 2022) can be used to obtain biobased products, biochar, and bioenergy from this feedstock. Heat transfer, chemical reactions, phase change, and mass transport occur in the processes described above (Pecha et al., 2019), which are frequently governed by the structure-composition ratio. Cow manure can be considered as lignocellulosic material. The lignocellulose material is described as a nanoscale hierarchical assembly of biopolymeric components of cellulose, hemicellulose, and lignin (Pecha et al., 2019). Carbohydrates, lipids, and minerals also can be found. A lot of information is found about the chemical methods to determine the lignocellulosic material composition, but less is known about the interaction between the structural parameters, and electrical properties such as complex conductivity. The present work focuses on the charge transport mechanism, and structure-conductivity ratio for cow manure, with the intention of a deeper understanding of the nature of this type of biomass for advanced applications.

2. Materials and Methods:

2.1 Collection and adaptation of biomass

Samples of cow manure were collected in San Juan de Betulia corregimiento of Albania, Sucre, Colombia. They were dried for 24h at a temperature of 45°C to remove physically adsorbed water and preserve the sample structure for X-ray diffraction (XRD) analysis. It was ground in an endless screw mill and fractions were separated into ASTM certified mesh 20, 30, 40, 60, and bottoms. Samples were labeled as 20, 30, 40, 60, and bottom.

2.2 Crystallographic analysis of bovine manure fractions

All X-ray diffraction (XRD) patterns of the powder samples were performed at room temperature with a Brag-Brentano focusing geometry on a RIGAKU MINIFLEX II diffractometer (Rigaku Company, Tokyo, Japan), using CuKα radiation at 30 kV. and 15 mA with a sweep rate of 2° (5 θ min−1 , sampling width of 0.01° (2θ), and between 3° and 50◦ (2θ).

2.3 Analysis of electrical properties of cow manure fractions

The samples in powder form were measured at a temperature of 18°C and ambient humidity. Data was recorded over a frequency range of 10 MHz to 0.1 Hz with a voltage amplitude of 100 mVrms and 0 DC bias in a Solartron 1260 coupled with a dielectric interface Solartron 1294. The samples were positioned in a special Solartron 12962A cell for the measurement of powder and liquid samples. The two-point method was used in bronze/sample/bronze configuration, using the methodology described by (Aguila Rodriguez et al., 2019; Arias et al., 2019a). From the impedance spectroscopy data, complex conductivity was calculated.

3. Results and Discussion

3.1 Structural Results

The fraction of bovine manure retained in mesh 20 (Figure 1) presented a diffraction peak located between 20 and 25° 2θ centered around 21.70°2θ and an additional diffraction peak located at 26.35° 2θ and corresponding to interplanar spacings of 4.09Å and 3.38 A. For the fractions retained in mesh 30 (Figure 1) there is a displacement of the first diffraction peak towards 21.98° (4.04 Å) and 26.45° (3.36 Å) 2θ. For the material retained in mesh 40 (Figure 1) there were diffraction peaks located at 21.41°, 25.5°, 36.22° 2θ with interplanar spacings of 4.15 Å, 3.49 Å and 2.48 Å, while for the material retained in the mesh (Figure 4) the representative diffraction peaks were located at 21.56°, 26.49°, 36.30°2θ with interplanar spacings of 4.12 Å, 3.36 Å, and 2.47 Å respectively. Finally, the backgrounds (Figure 1) presented diffraction peaks located at 21.70°, 25.93°, 36.51° 2θ with interplanar spacings of 4.09 Å, 3.43 Å, and 2.46 Å. When the diffraction patterns of all the bovine manure fractions were compared (Figure 4), an increase in the intensity of the diffraction peaks located at a high angle and a displacement of the diffraction signal of the diffraction peak located around 21 was observed. ° 2θ. Similarly, there was an increase in the intensity of the diffraction peak located at 21.98° (4.04 Å), which suggests a higher atomic density in that diffraction plane.

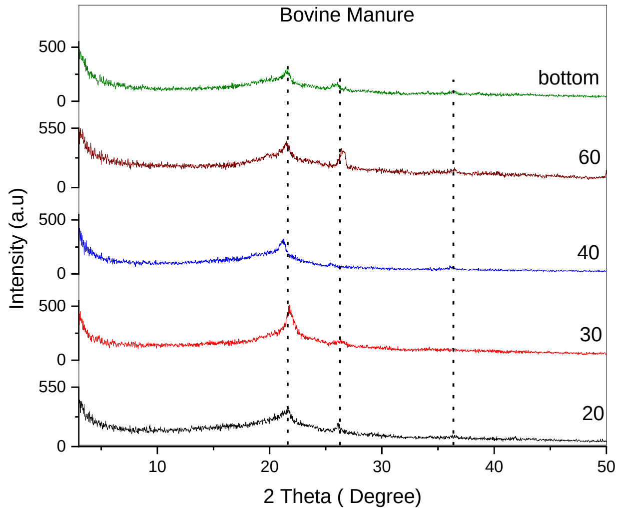

Figure 1. X-ray diffraction patterns for the bovine manure fractions analyzed.

The diffraction patterns found for the analyzed samples correspond to hemicellulose and cellulose(O'Sullivan, 1997) The peak located around 36° represents cellobiose chains.

The crystallinity indices for cellulose are presented in Table 1

mesh	% crystallinity
20	79.8
30	86.6
40	73.1
60	61.6
bottom	73.4

The percentage of crystallinity was calculated based on the equation(Tolosa et al., 2014).

$$\%\,Crystallinity = \frac{I_{am} - I_{002}}{I_{002}}$$

Where

I_{am} : Intensity of the amorphous phase,

I_{002} :Intensity of the diffraction plane (002) of the cellulose.

According to the results obtained, the lowest percentage of crystallinity is obtained in the material retained in the 60 mesh, so it would be an appropriate material for transformation since it is expected that with the decrease in crystallinity, the access points for chemical transformation will increase. The presence of lignin is not ruled out, however, additional tests are required.

Electrical analysis by impedance spectroscopy

To visualize the electrical response, it is decided to graph the real component of the complex conductivity as shown in figure 2. The conductivity data was obtained from impedance spectroscopy data as it is reported by Arias, et.al.,(Arias et al., 2019a; Giraldo et al., 2017) The conductivity of the samples increases as the frequency of the applied electric field increases, following an exponential trend that follows the universal law of Jonhscher (Arias et al., 2019b). At low frequency (below 100 Hz) the conductivity follows a plateau trend. Considering the molecular structure of cellulose, which in this case is the main component in the samples analyzed (See Figure 1), it is suggested that the terminal hydroxyl groups are involved in the behavior at high frequency, which are the ones with the greatest mobility, while at low frequency, a phenomenon of vehicular proton conduction (Kreuer et al., 1982) may occur between the cellulose and holocellulose molecules and of the Grothus type (Farrell & Zanni, 2019) between the hydrogen bonds of the molecule itself that is generated when the electronic clouds are deformed and the bonds in response to the applied electric field.

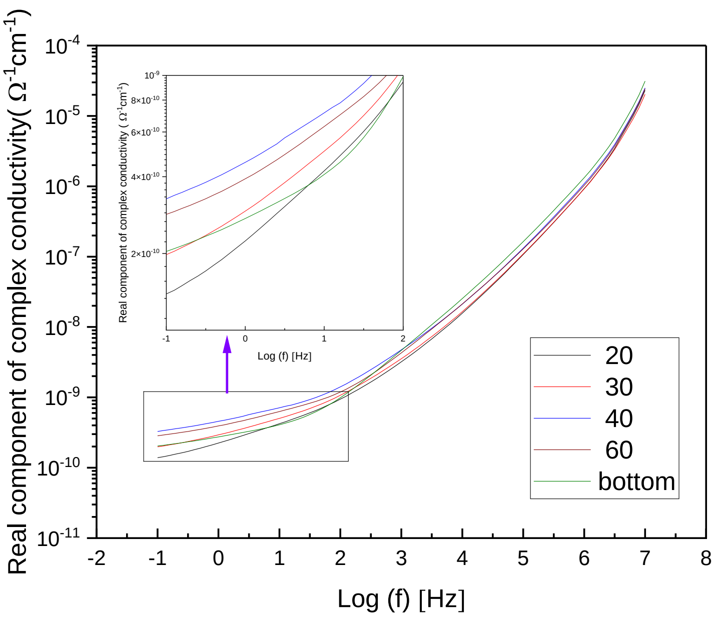

Figure 2. Effect of average particle size on the behavior of complex conductivity for dry bovine manure

As a summary of the conductivity values, the two extreme frequencies were taken: 01. Hz and 10MHz as presented in Table 2.

Table 2. Effect of particle size on actual conductivity

Mesh	Real conductivity at 0.1Hz	Real conductivity at 10MHz
20	1.39×10^{-10}	2.31×10^{-5}
30	1.98×10^{-10}	2.04×10^{-5}
40	3.28×10^{-10}	2.59×10^{-5}
60	2.85×10^{-10}	2.50×10^{-5}
bottom	2.04×10^{-10}	3.12×10^{-5}

The highest conductivity at low frequency was obtained with the 40 mesh, while at high frequency the highest conductivity occurred in the bottom fraction of bovine manure. The foregoing is understandable if it is placed in the context that the smaller the particle size there is greater the surface area, so it is possible that there are a greater number of hydroxyl molecules available to react to the electric field.

Conclusion

Cellulose is the main biopolymer found in cow manure. Molecular association with hemicellulose, lignin alters the AC conductivity. There was a crystallinity index-conductivity ratio. The foregoing is understandable if it is placed in the context that the smaller the particle size there is greater the surface area, so it is possible that there are a greater number of hydroxyl molecules available to react to the electric field.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Aguila Rodriguez, G., Arias Duque, N. P., Gonzalez Sanchez, B. E., Sandoval Gonzalez, O. O., Giraldo Osorio, O. H., Trujillo Romero, C. J., Wilches Torres, M. A., & Flores Cuautle, J. J. A. (2019). Sugar Concentration Measurement System Using Radiofrequency Sensor. *Sensors (Basel, Switzerland)*, *19*(10). https://doi.org/10.3390/s19102354

Arias, N. P., Becerra, M. E., & Giraldo, O. (2019a). Structural and electrical studies for birnessite-type materials synthesized by solid-state reactions. *Nanomaterials*, *9*(8). https://doi.org/10.3390/nano9081156

Arias, N. P., Becerra, M. E., & Giraldo, O. (2019b). Structural and Electrical Studies for Birnessite-Type Materials Synthesized by Solid-State Reactions. *Nanomaterials*, *9*(8), 1156. https://www.mdpi.com/2079-4991/9/8/1156

Awasthi, M. K., Sarsaiya, S., Wainaina, S., Rajendran, K., Kumar, S., Quan, W., Duan, Y., Awasthi, S. K., Chen, H., Pandey, A., Zhang, Z., Jain, A., & Taherzadeh, M. J. (2019). A critical review of organic manure biorefinery models toward sustainable circular bioeconomy: Technological challenges, advancements, innovations, and future perspectives. *Renewable and Sustainable Energy Reviews*, *111*, 115–131. https://doi.org/https://doi.org/10.1016/j.rser.2019.05.017

dos Passos, J. S., Matayeva, A., & Biller, P. (2022). Synergies during hydrothermal liquefaction of cow manure and wheat straw. *Journal of Environmental Chemical Engineering*, *10*(5), 108181. https://doi.org/https://doi.org/10.1016/j.jece.2022.108181

Farrell, K. M., & Zanni, M. T. (2019). Observing Aqueous Proton Transfer Dynamics. *ACS Central Science*, *5*(7), 1114–1116. https://doi.org/10.1021/acscentsci.9b00603

Giraldo, O., Arias, N. P., & Becerra, M. E. (2017). Electrical properties of TiO<inf>2</inf>-pillared bidimensional manganese oxides. *Applied Clay Science*, *141*. https://doi.org/10.1016/j.clay.2017.02.019

Goldfarb, J. L., Hubble, A. H., Ma, Q., Volpe, M., Severini, G., Andreottola, G., & Fiori, L. (2022). Valorization of cow manure via hydrothermal carbonization for phosphorus recovery and adsorbents for water treatment. *Journal of Environmental Management*, *308*, 114561. https://doi.org/https://doi.org/10.1016/j.jenvman.2022.114561

Hamedi, B., Ghasemi Pirbalouti, A., & Rajabzadeh, F. (2022). Manures, vermicompost, and chemical fertilizer impacts on the yield and volatile compounds of the damask rose (Rosa damascena Mill.) flower petals. *Industrial Crops and Products*, *187*, 115470. https://doi.org/https://doi.org/10.1016/j.indcrop.2022.115470

Herwintono, Winaya, A., Khotimah, K., & Hidayati, A. (2020). Improvement of biogas quality product from dairy cow manure using NaOH and Ca(OH)2 absorbents on horizontal tube filtration system of mobile anaerobic digester. *Energy Reports*, *6*, 319–324. https://doi.org/https://doi.org/10.1016/j.egyr.2020.11.152

Huhtanen, P., Krizsan, S. J., & Ramin, M. (2021). A meta-analysis of faecal output and nutrient composition, and potential methane emission from manure of dairy cows. *Animal Feed Science and Technology*, *282*, 115120. https://doi.org/https://doi.org/10.1016/j.anifeedsci.2021.115120

Khoshnevisan, B., Duan, N., Tsapekos, P., Kumar, M., Liu, Z., Mohammadi, A., Angelidaki, I., Cw, D., Zhang, Z., Pan, J., Ma, L., Aghbashlo, M., Tabatabaei, M., & Liu, H. (2021). A critical review on livestock manure biorefinery technologies : Sustainability , challenges , and future perspectives. *Renewable and Sustainable Energy Reviews*, *135*. https://doi.org/10.1016/j.rser.2020.110033

Kreuer, K.-D., Rabenau, A., & Weppner, W. (1982). Vehicle Mechanism, A New Model for the Interpretation of the Conductivity of Fast Proton Conductors. *Angewandte Chemie International Edition in English*, *21*(3),

208–209. https://doi.org/https://doi.org/10.1002/anie.198202082
O'Sullivan, A. C. (1997). Cellulose: the structure slowly unravels. *Cellulose*, *4*(3), 173–207. https://doi.org/10.1023/A:1018431705579
Pecha, M. B., Arbelaez, J. I. M., Garcia-Perez, M., Chejne, F., & Ciesielski, P. N. (2019). Progress in understanding the four dominant intra-particle phenomena of lignocellulose pyrolysis: chemical reactions, heat transfer, mass transfer, and phase change. *Green Chemistry*, *21*(11), 2868–2898. https://doi.org/10.1039/C9GC00585D
Schott, C., Cunha, J. R., van der Weijden, R. D., & Buisman, C. (2023). Innovation in valorization of cow manure: Higher hydrolysis, methane production and increased phosphorus retention using UASB technology. *Chemical Engineering Journal*, *454*, 140294. https://doi.org/https://doi.org/10.1016/j.cej.2022.140294
Tolosa, R. A., Jimenez-Obando, G., Arias, N. P., Cardona, C. A., & Giraldo, O. (2014). Cementicious materials reinforcement using angustifolia kunth bamboo fiber covered with nanostructured manganese oxidex. *Industrial and Engineering Chemistry Research*, *53*(20). https://doi.org/10.1021/ie403958y
Valizadeh, S., Pyo, S., Kim, Y.-M., Hakimian, H., & Park, Y.-K. (2022). Production of aromatics fuel additives from catalytic pyrolysis of cow manure over HZSM-5, HBeta, and HY zeolites. *Chemical Engineering Journal*, *450*, 137971. https://doi.org/https://doi.org/10.1016/j.cej.2022.137971