CO2 ADSORPTION ON CHAR FROM RICH-PROTEIN ANIMAL WASTES AND PURE PROTEINS. A COMPARATIVE STUDY.

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ABSTRACT: Biogas generation through anaerobic digestion (AD) provides an interesting opportunity to valorize animal waste materials through energy production. However, some residues generated in intensive livestock areas, such as meat and bone meal (MBM), cannot be anaerobically digested. A more flexible integrated process is needed to valorize a wider range of residues. Other issues to be addressed in AD are gas upgrading requirements, the increasing costs and the adequate management of the digestate. The high concentration of CO2 in biogas results in a low caloric value, making it mandatory to reduce the CO2 levels. The obtention of low-cost adsorbent materials for CO2 removal, preferably obtained from waste materials, would be beneficial for biogas generation. Char is a potential low-cost adsorbent material. Its composition and quality are strongly dependent on the precursor and its production conditions. Chars from proteins show very different characteristics compared to those obtained from the more commonly studied lignocellulosic residues. More specifically, chars obtained from digested manure and MBM (as rich-protein animal wastes) have a high nitrogen content, which could increase their CO2 adsorption capability if the nitrogen-functional groups contribute to surface basicity. In the current study, the CO2 uptake properties of chars prepared by pyrolysis at three different temperatures of two animal wastes, digested manure and MBM, and two proteins, collagen and soybean protein (considered as representative model compounds of the proteins found in these residues) have been investigated and compared. The CO2 adsorption capacities at room temperature have been measured with a TGA apparatus and the stability and regenerability of all char samples have been determined. The CO2 adsorption capacities of chars from both proteins were found to be very similar (up to 40 mg/g for the chars prepared at 750 ºC). Despite the lower BET surface area of the proteins chars (in the range of 1 m2/g measured with N2 adsorption), their CO2 adsorption capacities was found to be double to those obtained from animal wastes. The preliminary data in this study might be explained with a ultramicroporous texture, but additional work is needed to support this idea.

*Keywords: CO2 adsorption capacity, collagen char, soybean protein char, manure char and meat and bone meal char*

1. INTRODUCTION

Biogas technology has been actively promoted within the framework of the objectives of EU for the period 2010 to 2030 in order to increase the use of renewable energies and to decrease the emissions of greenhouse gases. Farming and intensive livestock are very important sectors in which the installed capacity of biogas generation can be increased. Anaerobic digestion (AD) or co-digestion of various animal waste materials produced in these sectors presents an interesting opportunity for valorization by means of energy generation. However, the economic feasability of the process has hindered its widespread development. Successful AD requires the proccessing of adequate residues under specific operating conditions, so not all residues can be biologically degraded, which reduces the flexibility of the feed composition (Ugwu & Enweremadu, 2020). While manure is a waste material suitable for AD, this is not the case for other residues produced in intensive livestock areas, e.g. meat and bone meal (MBM). Therefore, a more flexible integrated process is needed to valorize the entire range of residues produced in agricultural areas. Another issue to be considered is that raw biogas does not fulfill certain specifications for generating electricity directly. This makes some upgrading neccesary, which adds significantly to the costs. Finally, the digestate from AD needs adequate management due to environmental reasons.

Biogas is a complex mixture of CH4 and large amounts of CO2 (25 – 50%) as well as other undesired gases. The high concentration of CO2 results in a low heating value of the raw biogas. Therefore, CO2 has to be removed as part of the biogas upgrading (Ullah Khan et al., 2017). Among current commercial technologies for biogas cleaning, adsorption with activated carbon substantially increases the costs of the AD process, resulting in a severe burdon for the implementation of the process into intensive livestock farming. The high costs of biogas treatment are caused by the relatively high price of activated carbon and also by its regeneration process. Consequently, there is an increasing interest in identifying low-cost adsorbent materials, preferably obtainable from waste materials (Mulu et al., 2021). The idea of integrating the pyrolysis of AD digestate, possibly mixed with additional residues such as MBM, for onsite char production, presents a promising approach to implement biomass treatment through anaerobic digestion into livestock farming. AD could benefit from the different products generated in the pyrolysis process (Chen et al., 2021; Sánchez-Sánchez et al., 2018; Wu et al., 2020).

Char is generally considered a low-cost adsorbent material for treating gaseous effluents, although char composition and quality strongly vary depending on the starting material and process conditions (Yadav & Jagadevan, 2020). Despite the lower surface area of char produced from biomass wastes compared to that of activated carbon, several studies on CO2 removal from biogas have shown that char obtained from biomass wastes, without any activation step, can be an effective adsorbent. However, there is little information in the literature regarding the properties of chars produced via pyrolysis of digested manure and MBM. Both, digested manure and MBM, are rich-protein animal wastes and the resulting chars will be specially characterized by high nitrogen content. This could make these materials very suitable for CO2 adsorption. Previous research work have observed that nitrogen, specifically in form of pyrrolic nitrogen, acts as active adsorption sites with a high affinity for CO2 adsorption (Leng et al., 2019; Zhang et al., 2013).

The composition of the animal wastes will influence the morphological structure and the surface chemistry of the char obtained so, due to the variability in this composition, the experimental results for adsorption capacities of chars obtained from specific animal wastes cannot be extrapolate to other wastes. This calls for the need to develop a more thorough understanding of the CO2 removal process using char from animal wastes. In this context, a study of the CO2 adsorption capacity of chars generated from the main macro-components of animal wastes should be helpful to understand individual influences. Such a study needs to include chars produced from proteins, one of the major components of animal wastes, which distinguishes this type of waste material from other more commonly studied lignocellulosic residues. When comparing MBM and digested manure, the differences between the proteins present in them should also be considered. Thus, collagen, an animal protein, is the major constituent of MBM and soybean protein is a plant-based protein that could be considered as a representative protein found in digested manure.

In the current study, the CO2 adsorption capacities of chars prepared by pyrolysis of two animal wastes, digested manure and MBM, and two types of proteins, collagen and soybean protein, were investigated at room temperature and the results were compared. Specific objetives of this work were to (1) determine CO2 isotherm for the chars at room temperature; (2) analyze the effect of the raw material characteristics and pyrolysis temperature on the CO2 adsorption capacity and (3) test the reversibility of CO2 adsorption after regeneration at increased temperature.

1. EXPERIMENTAL

2.1 Char production

Two protein-rich animal wastes, co-digested manure (DM) and meat and bone meal (MBM), and two types of proteins, soybean protein (SP) and collagen (C), were used as feedstock for char production. The DM, supplied by the HTN biogas company (Spain), contains co-digested cattle manure and agro-industry residues. The material was oven-dried after receiving and stored. The MBM was supplied by the Spanish company Residuos Aragón S.A. once the prion that provokes the Bovine Spongiform Encephalopathy had been destroyed. The two proteins, SP and C, were commercial products acquired in a drugstore.

The raw materials were pyrolyzed in a fixed bed reactor of 2-3 g capacity in N2 atmosphere (50 mLSTP/min) at three different final temperatures (350, 550 and 750 ºC). A heating rate of 10 ºC/min was applied and the final temperature was kept for about 60 min. All char samples were crushed and sieved (particle size 0.025-0.063 mm) before characterization. More detailed information about the char production procedure has been reported in the work “*Pyrolysis of two different kinds of proteins: collagen and soybean protein. Analysis of their contribution on the pyrolysis of rich protein animal wastes*”, which is also included in: *Proceedings of the 18th International Symposium on Waste Management and Sustainable Landfilling*.

In the following, the char samples (a total of 12 samples) are named as a combination of letters related to the raw material used (DM, MBM, SP and C) followed by a number indicating the final pyrolysis temperature. For example, DM350 refers to the char prepared by pyrolysis of co-digested manure at 350 ºC.

2.2 Char characterization

Char samples obtained in the pyrolysis of the four materials were characterized in terms of chemical composition (elemental analysis) and surface chemistry (FTIR spectroscopy and textural properties) in order to explain the results observed for CO2 adsorption capacities. The elemental analysis was performed with a Truspec-CHN® (LECO) Elemental Analyser. Surface functional groups on the chars were identified by Attenuated Total Reflection-Fourier Transform Infra-Red (ATR-FTIR) spectroscopy analysis, using an Agilent Cary 600 FTIR spectrometer, with a resolution of 4 cm-1 in the wavelength range of 4000 - 400 cm-1 (medium IR region). Char surface areas were measured with a Quantachrome Autosorb® 6 Surface Area and Pore Size Analyzer. The samples were degassed at 523 K for 15 h prior to surface area analysis. Both N2 and CO2 adsorption isotherms (at 77 K and 273 K, respectively) were evaluated.

2.3 CO2 adsorption procedure

The CO2 adsorption capacity of the char samples was examined by thermogravimetric analysis (TGA) with a Netzsch STA 449 Jupiter® thermobalance. Adsorption was evaluated at room temperature and atmospheric pressure. About 50 mg of ground and sieved char sample (particle size of 0.025-0.063 mm) was firstly degassed at 250 ºC for one hour in a N2 stream (100 mLSTP/min). After cooled down to 25 ºC, the sample was exposed to various CO2/N2 mixtures (CO2 concentration ranging 2-83 vol. %) and the change in sample weight was measured (N2 adsorption on the char samples was considered negligible). The use of 20 mLSTP/min of N2 as protective gas flow in the TGA apparatus prevented the study of adsorption of pure CO2. Once the gas flow was switched to a selected CO2 composition, the sample was held at 25 ºC for 50 min to establish equilibrium between CO2 in the gas phase and on the surface. Adsorption of CO2 in these chars occurs slowly and in some cases the weight was still slightly increasing after 50 min, so final CO2 adsorption capacities could be somewhat higher than measured here. The adsorption tests at different CO2 mole fractions were divided into three sets. Between these sets, the sample was again degassed by raising the temperature by 10 ºC/min up to 150 ºC (desorption branch) and afterwards lowered to 25 oC (adsorption branch) in N2 atmosphere. This procedure tests for chemisorption or alternatively the reversibility of CO2 adsorption. Several CO2 mole fractions were tested more than once to obtain information on the repeatability of the measurements.

The CO2 adsorption capacity of chars (mg CO2/g char) for each CO2 partial pressure was calculated from the weight gain relative to the weight in pure N2 atmosphere.

1. RESULTS AND DISCUSSION

**3.1. Char characterization**

Char samples obtained in the pyrolysis of the four materials were characterized in terms of chemical composition (elemental analysis) and surface chemistry (FTIR spectroscopy and surface area measurement) in order to explain the results observed for CO2 adsorption capacities. A more detailed discussion about these characterization results can be found in the work “*Pyrolysis of two different kinds of proteins: collagen and soybean protein. Analysis of their contribution on the pyrolysis of rich protein animal wastes*”, which is also included in: *Proceedings of the 18th International Symposium on Waste Management and Sustainable Landfilling*.

*3.3.1 Elemental Composition*

Important differences have been found when comparing the elemental analysis of the residues and the pure proteins (Table 1). On an ‘as received basis’, chars obtained from the proteins are much richer in C and N than the residues, mainly because of ash dilution in the wastes. The ratio N/C is also higher in the proteins chars (quite similar values in both cases), followed by the meat and bone meal chars. The N/C ratio in the digested manure chars is about 3-4 times lower than in meat and bone meal chars (for instance, 0.03 in DM750 vs. 0.12 in MBM750). A slight downward trend is observed in N/C ratio when increasing the pyrolysis temperature.

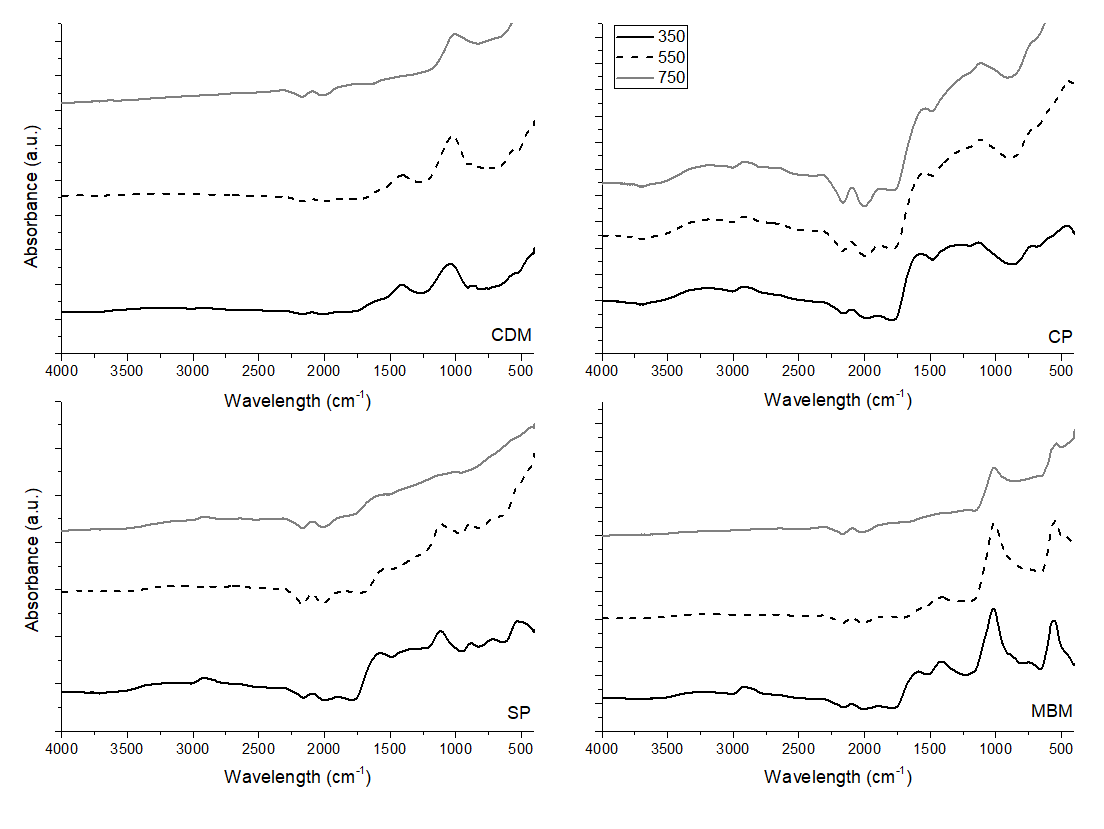
Table 1. Elemental analysis data of pyrolysis chars

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **Chars produced at 350 ºC** | | | **Chars produced at 550 ºC** | | | **Chars produced at 750 ºC** | | |
|  | **C (%)** | **H (%)** | **N (%)** | **C (%)** | **H (%)** | **N (%)** | **C (%)** | **H (%)** | **N (%)** |
| **Collagene** | 56.7±0.7 | 4.50±0.05 | 14.6±0.2 | 65±1 | 2.6±0.2 | 14.0±0.2 | 61±3 | 1.2±0.1 | 10.5±0.5 |
| **Soybean protein** | 58±2 | 4.90±0.03 | 13.7±0.9 | 46±2 | 2.60±0.02 | 10.1±0.1 | 56.0±0.8 | 1.3±0.1 | 9.5±0.1 |
| **Meat and bone meal** | 41±1 | 3.7±0.3 | 8.4±0.4 | 39.0±0.9 | 1.5±0.2 | 6.5±0.1 | 36.4±0.1 | 0.68±0.01 | 4.9±0.1 |
| **Digested manure** | 32.6 | 2.5 | 2.1 | 37.0 | 1.5 | 2.3 | 36.2 | 0.5 | 1.2 |

The CO2 adsorption capacity of chars can be enhanced by increasing the alkalinity of its surface (Dissanayake et al., 2020). Nitrogen-containing functional groups (e.g., amide, imide, pyridinic, pyrrolic, and lactam groups) can contribute to the surface basicity of biochars and promote the CO2 adsorption (Qiao et al., 2020). Therefore, biomass wastes with high protein content could be considered as potential precursors for low cost CO2 adsorbent.

*3.3.2 ATR-FTIR*

The nature of the functional groups present on a solid surface can be analyzed by ATR-FTIR (Figure 1). No peaks related to OH-groups (3400-3200 cm-1) are found in the spectra of the chars, with the exception of the chars obtained from collagen at the three pyrolysis temperatures and the soybean char prepared at 350 ºC. The expected peak assigned to amino group (N-H) at about 3250 cm-1 is not found in any of the char spectra, which points to its destruction during pyrolysis. The peaks around 1625 and 1520 cm-1 represent the amide groups and appear in chars obtained from proteins and to a lesser extent in the low-temperature char from MBM. The peaks between 2400 and 2200 cm-1 can be related to nitriles groups. They remain during pyrolysis for all the feedstocks with slightly higher intensity at higher temperatures. These peaks are the only ones related to nitrogenous groups that can be observed in DM chars (which also showed the lowest N content in the elemental analysis). Chars from collagen seem to be the samples with the highest content of nitrogen functionalities and chars from DM the samples with the lowest one.



**a)**

**c)**

**b)**

**d)**

Figure 1. FTIR spectra for the chars obtained at the three different pyrolysis temperatures from: a) Co-digested manure, b) Collagen, c) Soybean protein, d) Meat and bone meal.

*3.3.3 Surface area*

Four N2 adsorption isotherms for representative chars are shown in Figure 2, each representing one of the raw materials. These data were taken with the standard setting, meaning that the P/Po range is 0.02 to 0.99. This procedure does not return complete isotherms, but only the high pressure part. It is important to note that the volume ranges of the isotherms differ significantly: they are much higher for chars from the wastes (Figures 2a and 2b) than for those from the proteins (Figures 2c and 2d). These results clearly show that N2 adsorption hardly took place in proteins chars. Proteins melting during thermal treatment (at temperatures around 250 ºC) seems to be a key point in the final structure of the produced chars, as a poor porosity structure in the form of macropores, mesopores or wider micropores has been found with N2 adsorption tests.

Although the initial part of the isotherm at lower relative pressures is missing, isotherms of DM and MBM can be included as Type IV according to IUPAC classification (Sing, 1982). Most of the isoterms showed pronounced hysteresis loops, indicating that the adsorption and/or desorption branches are not in equilibrium. These hysteresis loops are usually related to condensation phenomena occurring in mesopores.

**b)**

**a)**

**d)**

**c)**

Figure 2. N2 adsorption isotherms for: (a) DM750, (b) MBM750, (c) SP750, (d) C750.

The multi-point BET analysis was applied to N2 adsorption data, obtaining the BET surface areas (SBET) summarized in Table 2. As commented, soybean protein and collagene hardly show BET area. Small values for the BET surface area have been obtained for digested manure and meat and bone meal, much smaller than usually found in activated carbons. Multi-point BET analyses of DM750 char resulted in a negative C value in any range of P/Po, so SBET could not be estimated for this sample. The t-plot based on the de-Boer equation has also been used to calculate micropore surface area. With this analysis, micropores are proved to be present in MBM550 and MBM750, whose micropore area reached 28% and 9% of total SBET, respectively.

Table 2. Surface area by BET-method (N2 adsorption at 77 K).

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **DM350:** | 6 m2/g | **MBM350:** | 5 m2/g | **C350:** | 1 m2/g | SP350: | 6 m2/g |
| **DM550:** | 16 m2/g | **MBM550:** | 28 m2/g | **C550:** | 1 m2/g | SP550: | 1 m2/g |
| **DM750:** | --- | **MBM750:** | 29 m2/g | **C750:** | 1 m2/g | SP750: | 1 m2/g |

3.2. CO2 uptake properties

The CO2 adsorption performance of the char samples was examined using thermogravimetric methods. The adsorption capacities for the sorbent materials can be explained using the adsorption isotherm plots: the more the adsorbed volume, the higher will be the adsorption capacity.

Figure 3 shows the experimental data of CO2 adsorption isotherms at 25 ºC.

Figure 3. Experimental CO2 adsorption isotherms (filled symbols) measured at 25 ºC in the TGA apparatus and Langmuir (continuous lines) and Freundlich fits (dot lines).

Two well-known isotherm models, the Langmuir and the Freundlich adsorption isotherms, were used to analyze the experimental data for the adsorption of CO2 on the chars. Mathematically, all profiles are reasonably well represented by either Langmuir or Freundlich models in the P/Po range studied (coefficient of determination of multiple regression: 0.961 < R2 < 0.995), so this mathematical analysis is not sufficient information to conclude if CO2 adsorption occurs on a monolayer homogeneous surface (as the Langmuir model assumes) or on a multilayered heterogeneous surface (as the Freundlich model refers to). Both analyses assume the relevance of the surface area concept to explain CO2 adsorption on chars and the reasonably good fits do not contradict this assumption.

CO2 uptake data for all chars (at the highest concentration of CO2: 83 vol. %) are summarized in Figure 4. Comparing these data, it can be observed that proteins chars, especially those from collagene, show higher adsorption capacity than the waste biochars.

The figures also indicate that the mass of CO2 adsorbed is higher for chars prepared at high temperature, except for MBM chars, whose maximum in the CO2 adsorption capacity is found at a pyrolysis temperature of 550 ºC. It is to note that the CO2 adsorption performance of chars changes much more between the pyrolysis temperature of 350 and 550 ºC than between 550 and 750 ºC.

CO2 adsorption capacities of proteins chars prepared at 750 ºC are essentially twice than those of their related wastes (40 vs. 20 mg CO2/g char), while these differences are, in general, less significant in the chars prepared at lower pyrolysis temperatures. This means that increasing the pyrolysis temperature especially benefits the CO2 uptake properties of the two studied protein chars, while the impact on the waste chars is smaller.

Figure 4. CO2 uptake of char samples at 25 ºC (gas mixture with 83 % vol. CO2).

In order to explain the differences in the CO2 adsorption capacities of the chars, both the surface basicity and porous texture should be considered. The increase of pyrolysis temperature leads to a reduction of N content in the chars (Table 1), thus reducing the contribution of nitrogen-containing functional groups to surface basicity. Therefore, the positive effect of pyrolysis temperature on the CO2 adsorption capacity of chars seems to be more related to changes in the porous texture.

The superior performance of the proteins chars produced at 750 ºC can not be explained by solely considering either the SBET (which was almost zero in most cases) or the N content (which decreased with pyrolysis temperature). Additional analyses have been done based on other concepts such as the TVFM (theory for the volume filling of micropores) approach by Dubinin (Dubinin, 1989). CO2 adsorption isotherms at 273 K were examined using the Dubinin-Radushkevich (DR) equation at a low relative pressure (P/Po < 0.03). The micropore volume and average pore width results calculated according to this method are shown in Table 3. Narrower micropores were detected for higher pyrolysis temperatures. The good linearity in DR-plots is consistent with the micropore filling model for CO2 adsorption in narrow micropores (ultramicropores), which could not be detected by single N2 adsorption because of the restricted diffusion of N2 into very narrow micropores at low temperatures and pressures (Jagiello et al., 2019). The origin of such ultramicroporous structure could be the release of gas molecules through the thermoplastic phase occurring during the pyrolysis of proteins.

Table 3. Micropore volume (Vmp) and average pore width (Dp) according to DR-method (CO2 adsorption at 273 K).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **Vmp (cm3STP/g)** | **Dp (nm)** |  | **Vmp (cm3STP/g)** | **Dp (nm)** |
| **C350:** | 0.042 | 0.989 | **SP350:** | 0.052 | 1.012 |
| **C550:** | 0.108 | 0.759 | **SP550:** | 0.088 | 0.746 |
| **C750:** | 0.083 | 0.713 | **SP750:** | 0.052 | 0.724 |

Therefore, according to these results, biochars obtained from biomass wastes rich in proteins could be appropriate for the adsorption of small gas molecules but not for the larger ones because of the molecular size exclusion.

**3.3. Regeneration of char after CO2 adsorption**

Three adsorption-desorption cycles were measured and regeneration tests were conducted after each cycle by heating the adsorbent up to 150 °C under N2 gas flow. Once cooled to 25 ºC, the adsorbent after regeneration was reused for CO2 tests in the next cycle. Figure 4 summarizes CO2 uptake results for chars for the first, second and third cycle of adsorption-regeneration. Quite similar results are observed, especially in cycles #2 and #3, which points to a reversible CO2 adsorption process.

Table 4. Cyclic adsorption-desorption behaviour of char samples (mg CO2/g char).

|  |  |  |  |
| --- | --- | --- | --- |
|  | **Cycle #1** | **Cycle #2** | **Cycle #3** |
| **S350** | 9.5 | 9.2 | 9.0 |
| **S550** | 29.0 | 27.8 | 28.1 |
| **S750** | 38.0 | 37.0 | 36.7 |
| **DM350** | 8.5 | 7.4 | 7.8 |
| **DM550** | 17.8 | 15.4 | 15.7 |
| **DM750** | 19.5 | 19.2 | 19.1 |
| **C350** | 11.0 | 10.4 | 10.3 |
| **C550** | 32.8 | 31.4 | 31.9 |
| **C750** | 41.0 | 38.8 | 39.2 |
| **MBM350** | 5.8 | 4.4 | -- |
| **MBM350** | 26.8 | 26.4 | -- |
| **MBM750** | 21.1 | 18.2 | -- |

1. CONCLUSIONS

The CO2 adsorption potential of chars produced from pyrolysis at 350-750ºC of protein-rich animal wastes (co-digested manure and meat and bone meal) and their most representative proteins (soybean protein and collagene) has been analyzed in a thermogravimetric apparatus (TGA). Adsorption isotherms at 25ºC have been determined and tried to correlate with char characterization results (elemental analysis, FTIR technique and textural properties) to improve the fundamental understanding of relation between composition and CO2 adsorption properties of final char material.

Proteins chars show higher CO2 adsorption capacity than their related waste biochars. The superior performance of the proteins chars, especially those produced at 750 ºC, can not be explained by solely considering either the SBET (which was almost zero in most cases when involving N2-adsorption) or the N content (which decreased with pyrolysis temperature). Other concepts such as the TVFM (theory for the volume filling of micropores) approach by Dubinin should be considered for a better interpretation of the results.

It is still not clear what is needed to produce an efficient CO2-adsorbing char (without further activation steps), pointing that more work is needed to study the interactions with other macro-components present in the animal wastes.

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