

Review

# Pretreatment of Animal Manure Biomass to Improve Biogas Production: A Review

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**Abstract:** The objective of this research is to present a review of the current technologies and pretreatments used in the fermentation of cow, pig and poultry manure. Pretreatment techniques were classified into physical, chemical, physicochemical, and biological groups. Various aspects of these different pretreatment approaches are discussed in this review. The advantages and disadvantages of its applicability are highlighted since the effects of pretreatments are complex and generally depend on the characteristics of the animal manure and the operational parameters. Biological pretreatments were shown to improve methane production from animal manure by 74%, chemical pretreatments by 45%, heat pretreatments by 41% and physical pretreatments by 30%. In general, pretreatments improve anaerobic digestion of the lignocellulosic content of animal manure and, therefore, increase methane yield.

**Keywords:** anaerobic digestion; biogas; degradation; lignocellulose; manure; pretreatments

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## 1. Introduction

Excessive organic waste agricultural accumulation, especially animal manure, can be a source of contamination of land, water and air [1]. In this sense, there are many efforts to transform these wastes into clean and renewable energy, such as the use of anaerobic digestion (AD) to produce biogas. Animal manure is considered very attractive for the production of renewable energy, since it is a natural resource that can additionally replace industrial fertilizers and improve soil fertility [2]. However, manure has some limitations, since it has a low C/N ratio, little volatile solids (VS) and many materials of difficult degradability, such as lignocellulosic biomass making biogas production unsatisfactory [3–6]. This limitation results from cattle diet based on pasture residues that include a significant content of lignocellulosic materials [7,8]. Hence, in recent years, there has been great interest on the part of many researchers in improving AD animal manure processes [9,10].

The hydrolysis stage is one of the limiting factors of AD due to the difficult degradation of lignocellulosic materials [11]. Generally, these materials are composed of cellulose, hemicellulose, lignin, and various inorganic materials [12]. Cellulose represents between 40 and 50%, hemicelluloses between 25 and 35% and lignin between 15 and 20%; materials that are extremely resistant to enzymatic digestion [13]. The conversion of lignocellulosic biomass residues, mainly from agricultural waste, municipal waste, animal manure, etc., into biofuels is very complex [14]. In many of these residues, lignin is usually the material that causes the most inconvenience in digestion [15]. It has been shown that the higher the lignin content, the greater the resistance of biomass to degradation [16].

Therefore, it is necessary to look for new technologies aimed at addressing the AD process to optimize it and eliminate the bottleneck generated in the hydrolysis process [17]. The proposed alternatives contemplate the inclusion of a pretreatment stage prior to the AD process [10].

Pretreating the substrate makes for a more efficient conversion of hardly degradable biomass, accelerating the hydrolysis process, and therefore improve biogas production [18]. However, each type of manure has its own biodegradability process, which makes the pretreatments that are proposed to optimize fermentation have their own specificity and are diverse.

A large number of investigations are focused on seeking pretreatments to improve the biogas production of agricultural residues such as cereals, pruning remains, sewage sludge, etc. However, in regard to animal manure, especially cow, pig and poultry, there are few studies in the literature examining their adaptability to anaerobic biodegradability. Hence, there is a special interest in compiling the most widely used pretreatment methods in the fermentation of livestock waste.

Pretreatments prepare the substrates to facilitate the action of microorganisms reducing size and molecular composition of the pretreated substrate, making it more accessible to bacterial consortia present in a reactor [19]. Atelge et al. [20] deem that pretreatments increase the substrate's surface area so that enzyme activity is enhanced, causing biomass de-crystallization resulting in increased digestibility [21]. In addition, pretreatments intensify porosity in the substrates, causing greater microbial accessibility [22]. Similarly, some pretreatments contribute to hemicellulose removal and lignin from the substrate; this elimination increases the accessibility to cellulose, facilitating the degradation process [21]. For these reasons, the development of new technologies and various methods for biomass pretreatment continue. Likewise, the applicability of different pretreatments cannot be generalized for all substrates since there is a lack of common and standardized protocols to evaluate their efficacy [23].

The objective of this review is to present the foundations and current states of various pretreatments applied to anaerobic digestion of cattle, pig and poultry livestock waste. The successes obtained and the existing difficulties of the techniques used in maximizing biogas production are highlighted. Moreover, the composition of the lignocellulosic material is described, giving an overview of its incidence in the hydrolysis phase of the AD process.

## 2. Hydrolysis in Anaerobic Digestion of Animal Waste

Relating the content of cellulose, hemicellulose and lignin present in animal manure with its methane production is very important, since through this it can be known which lignocellulosic component has the greatest influence on the biodegradability of the substrate. The AD process is clearly complex and depends on many factors; however, knowing the lignocellulosic composition of each type of manure, a type of pretreatment can be applied to each of them

Table 1 shows cow, pig and poultry manure residue fiber content mainly used in recent years. Recorded values show a high dispersion, although the same type of manure is compared. This is due to the fact that the digestibility of the animals is varied in the different parts of the world, which makes the percentages of lignocellulosic material vary with very wide ranges among themselves [24]. In the table, the methane production and the inoculum used in the anaerobic digestion process are also presented. In most investigations, sludge from wastewater treatment plants of various raw materials is used as inoculum. The inclusion of an inoculum has been key in the start-up of the digesters. The quality and quantity are determiners in defining the start-up period duration and digester performance, since this is where the active biomass grows and acquires vital properties necessary for organic matter removal, consequently reducing digestion time [25].

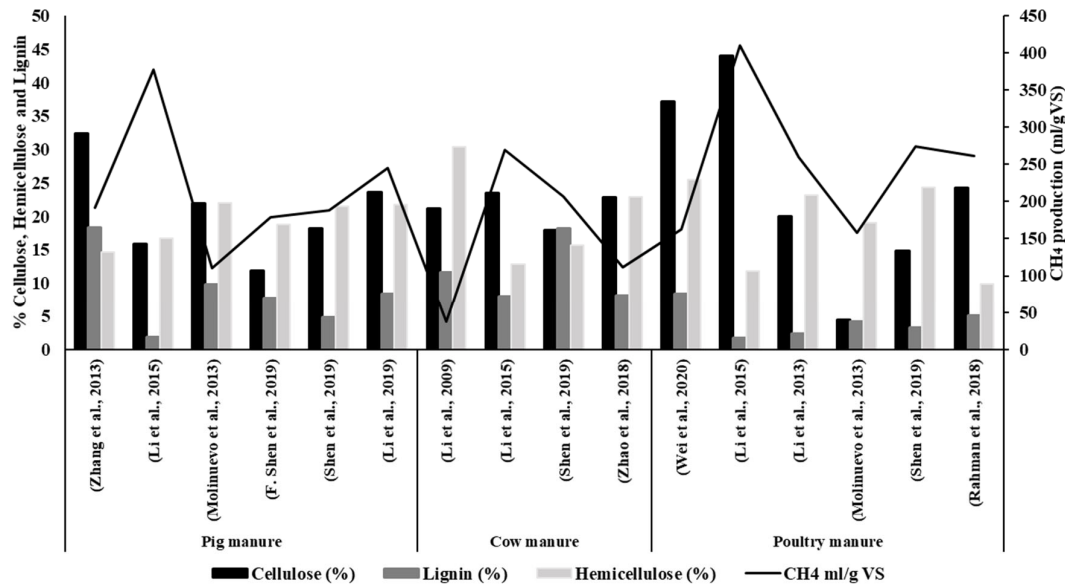
**Table 1.** Results of monodigestion of pig, cow and poultry manure with different fiber compositions.

Feedstock	Cellulose (%)	Lignin (%)	Hemicellulose (%)	CH <sub>4</sub> mL/g VS	Inoculum	References
Pig manure	32.4	18.4	14.6	191.4	a	[26]
Pig manure	15.9	1.8	16.7	377.0	b	[24]
Pig manure	22.0	9.8	22.0	111.0	b	[27]
Pig manure	11.9	7.7	18.8	178.7	b	[28]
Pig manure	18.2	4.8	21.5	187.7	b	[29]
Pig manure	23.6	8.4	21.7	245.1	b	[30]
Cow manure	21.2	11.6	30.4	37.5	c	[31]
Cow manure	23.5	8.0	12.8	270.0	b	[24]
Cow manure	17.9	18.2	15.7	206.9	b	[29]
Cow manure	22.9	8.1	22.9	112.1	d	[32]
Poultry manure	37.2	8.4	25.5	163.2	a	[33]
Poultry manure	44.0	1.7	11.8	410.0	a	[24]
Poultry manure	20.0	2.3	23.2	260.8	a	[34]
Poultry manure	4.4	4.2	19	158.0	a	[35]
Poultry manure	14.9	3.3	24.3	273.9	a	[29]
Poultry manure	24.3	5.1	9.9	261.7	e	[36]

Note: a: sludge from a beer treatment plant, b: sludge from an anaerobic digester from a waste water treatment plant (WWTP), c: sludge from a pig waste reactor, d: sludge from a corn straw silage reactor and pig manure, e: sludge from a digester (cow dung, wheat straw and grass).

In Table 1, pig manure presents averages of cellulose, hemicellulose and lignin of 20.67%, 19.22%, and 8.48%, respectively; cow manure, on the other hand, has ranges of 21.38%; 20.45% and 11.48%, respectively. Finally, poultry manure contains cellulose, hemicellulose and lignin of 24.13%, 18.95% and 4.17%, respectively. The lignocellulosic composition of other organic wastes is also similarly formed. Thus, for example, cereal residues contain 30–45% cellulose, 10–40% hemicellulose, and 5–25% lignin [37]. Lawn waste contains 25–39% cellulose, 17–32% hemicellulose, and 9–20% lignin [38]. Alternatively, fruit waste has varied compositions and depends mainly on the relative proportion of skin and seeds of individual sources [39].

Although the minor lignocellulosic component is lignin; this is the material that generates the most inconvenience in the digestion of animal manure. The highest percentage of lignin was registered in cow manure (9.8%), then in pig manure (8.5%) and finally in poultry manure (4.2%). As the value of lignin decreases, methane production increases both for cow manure and for pig and poultry manure (Figure 1), demonstrating that the recalcitrant content of lignin mostly inhibits methane production. Thus, the average value of methane production from the monodigestion of pig, cow and poultry manure is 215 mL/g VS, 168 mL/g VS, and 255 mL/g VS, respectively.



**Figure 1.** Production of methane from livestock residues and influence of cellulose, hemicellulose and lignin content.

The above-mentioned results have been carried out in batch digesters, using sewage sludge, sludge from a beer waste treatment plant and sludge from an anaerobic livestock waste digester. The results of the monodigestion of the latter are low; the reasons for its poor performance are diverse. For instance, the higher the lignan content, the greater the biomass resistance to degradation [16]. Additionally, because the concentration of volatile solids in animal manure is very low, it accounts for significantly reduced substrates production [11].

The conversion of cellulose and hemicellulose into energy also generates low efficiency in the production of biogas due to the intra and intermolecular hydrogen bonds of the hydroxyl groups, producing a supramolecular structure with a high degree of polymerization [16]. Thus, hydrogen bonding causes cellulose crystallinity to occur, making digestion difficult during enzymatic hydrolysis [40]. In short, the presence of lignocellulosic material affects the hydrolysis process, creating a barrier or shield that prevents the action of microorganisms in substrate degradation.

### 3. Pretreatments and Techniques to Improve the Digestion of Animal Manure

One of the techniques traditionally used to overcome the limitation of hydrolysis is the solubilization and degradation of the hemicellulosic and lignin parts of the substrate [41]. The objective of the pretreatment process is to eliminate lignin and hemicelluloses, reducing the amount of crystalline cellulose and increasing the porosity of lignocellulosic materials [42]. There are different types of pretreatments to remove lignocellulosic material, all of which are related through the use of physical, chemical, physicochemical, and biological procedures [43,44].

#### 3.1. Physical Pretreatments

Physical pretreatments break cells through physical force, allowing them to increase the surface area of the biomass by reducing particle size. This reduction in size can improve biomass accessibility and increase its susceptibility to microbial and enzymatic attacks, promoting biomass digestion during AD [21]. Furthermore, physical pretreatment does not produce secondary inhibitory substances, suggesting that they might be suitable for the production of methane or any other bioprocess. It is classified into two groups: mechanical, which includes milling and extrusion; and thermal [11,45].

In general, mechanical pretreatments and their combination with thermal ones cut, grind, and reduce cellulose crystallinity, but, above all, they reduce particle size, facilitating the activity of

microorganisms in the degradation of biomass [46]. These are highly effective methods, but their applicability is expensive and demands high energy, in addition to making extrapolation challenging on an industrial scale.

### 3.1.1. Mechanical Pretreatment

Milling is a pretreatment that reduces the crystallinity of the cellulose, increasing the digestibility of the particles [42]. The choice of techniques depends on the moisture content of the biomass [21]. However, milling has the limitation that it does not eliminate lignin, being an unsuitable option for those substrates that have a large amount of lignin [47]. Extrusion, on the other hand, is a method where compression and shear forces improve the degree of softening that causes greater access by microorganisms [11]. The duration of applicability of the pretreatment depends on the type of biomass treated, which means that its application cannot be standardized [45].

### 3.1.2. Heat Pretreatment

Thermal treatments consist of reaching temperatures between 150 and 250 °C. The most common treatments are usually cooking and radiation. Both require a closed and hermetic bottle that allows them to reach those temperatures.

Cooking or treatment with liquid hot water (LHW) consists of heating the manure while maintaining the liquid state of the water by increasing the pressure by 5 MPa [12,47]. In this pretreatment, hemicellulose is depolymerized and the products dissolve in the liquid phase, while cellulose is completely retained in the solid phase [48].

Radiation is usually with microwaves on wet manures or infrared on drier manures. One of the advantages of microwave irradiation is the degradation of lignocellulose materials into more brittle fibers and low molecular weight oligosaccharides; degradation that is obtained through the dissociation of glycoside bonds [42,49].

The application of heat has the disadvantage of compromising energy balance since many pretreatments demand high energy costs, as the degradation of lignin requires high temperatures to dissolve [50].

## 3.2. Physicochemical Pretreatments

### 3.2.1. Steam Explosion

This pretreatment consists of placing the biomass in a reactor with saturated steam under conditions of temperatures and pressure of 160–200 °C and 0.69–4.83 MPa, respectively [51]. Once the steam condenses and penetrates the pretreated biomass, it is suddenly depressurized. The glycosidic hemicellulose bonds are then broken and its solubilization occurs [52]. In this way, the pressure is gradually released and the steam expands through the lignocellulosic material of the organic matter, breaking the cell wall [53].

### 3.2.2. Plasma

Plasma pretreatment consists of applying ozone (O<sub>3</sub>) to the biomass composed of lignocellulosic materials. The application of ozone causes an alteration of the biomass and radioactive compounds such as HO and H<sub>2</sub>O<sub>2</sub> are generated. In this way, the interaction of these compounds in the biomass contributes to a degradation of the lignocellulosic materials and simpler compounds (such as glucose) are obtained as a product. In short, the surface of the pretreated biomass is altered and the action of the macro-organisms is facilitated, producing an acceleration of the hydrolysis process [52,54].

### 3.2.3. CO<sub>2</sub> Explosion

The application of CO<sub>2</sub> as pretreatment of biomass in the anaerobic digestion process is a process in which CO<sub>2</sub> is used as a green solvent to treat biomass before hydrolysis. Their procedure consists of applying CO<sub>2</sub> to the biomass in the presence of water to accelerate the enzymatic digestibility [55].

CO<sub>2</sub> acts as a solvent in the pretreated biomass transforming it into glucose through the enzymatic hydrolysis of cellulose from the exploited materials [56]. An upside of this pretreatment is that it requires little temperature and it is easy to separate the solvent from the pretreated biomass. Finally, it does not generate flammable or corrosive products in its applicability [47].

#### 3.2.4. Ammonia Fiber Expansion (AFEX)

In this pretreatment, the biomass is subjected to the application of ammonia at relatively high temperatures (90–100 °C) [12]. This process normally adds ammonia to a reactor containing lignocellulosic material at high pressure and temperature for approximately 30 min. Once the pretreatment has begun, the pressure is gradually decreased until the degradation of hemicellulose in oligomeric sugars is achieved [47]. An advantages of this pretreatment is that deacetylation of the pretreated material is achieved and, on the other hand, ammonia can be recovered for reuse in the next procedures. However, this pretreatment does not alter lignin, which makes the hydrolyzation of cellulose and hemicellulose possible [57].

### 3.3. Chemical Pretreatments

#### 3.3.1. Alkaline Hydrolysis

This pretreatment consists of adding alkaline compounds (NaOH, Ca (OH)<sub>2</sub>, NH<sub>3</sub>, etc.) to the biomass to accelerate the hydrolysis process. The choice of the type of alkaline solution is made based on cost and its possibility of recovery. Thus, for example, Ca(OH)<sub>2</sub> is the least expensive, and in addition calcium can be recovered in insoluble calcium carbonate by neutralizing calcium with carbon dioxide [47]. This pretreatment is very useful in the solubilization of lignin [58]. According to Janker et al. [59], NaOH causes the interruption of the hydrogen bond in cellulose and hemicellulose; breaking the ester bonds between lignin and xylan and causing the deprotonation of phenolic groups. Many researchers consider that the application of NaOH as a pretreatment generates better biomass digestibility results than the application of Ca(OH)<sub>2</sub> [11].

#### 3.3.2. Acid Hydrolysis

This pretreatment consists of treating the biomass at high and low temperatures with the following compounds: sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), hydrochloric acid (HCl), acetic acid (CH<sub>3</sub>COOH) and nitric acid (HNO<sub>3</sub>). Pretreatment can be performed with dilute acid (low concentration and high temperature) and with concentrated acid (high concentration and low temperature) [12]. The application of this pretreatment contributes to the elimination of lignin, causing better cellulose degradation by different enzymes and microorganisms. Li et al. [60] consider that acid pretreatment causes the interruption of van der Waals forces, hydrogen bonds and covalent bonds that hold the components of the biomass together, causing the solubilization of hemicellulose and the reduction in cellulose.

However, the main disadvantages of applying this pretreatment is the high cost of equipment resistant to corrosive acids, and the need to recover and recycle some chemicals or solvents [11]. Thus, the high cost of the necessary equipment and the need for additional energy for the thermal process make it unprofitable [61].

#### 3.3.3. Organosolv

This method is generally used to extract lignin from lignocellulosic raw materials. This extraction causes the cellulose fibers to be exposed to enzyme activity, causing further acceleration of the hydrolysis phase. This extraction exposes cellulose fibers to enzyme activity, inducing further acceleration of the hydrolysis phase. Furthermore, aqueous organic solvents (methanol, acetone, ethanol, and ethylene glycol) can be used to remove or decompose part of the hemicellulose [62]. The use of these solvents has the advantage of being easy to recover and recycle; its recovery can be carried out through a distillation process once the pretreatment has finished. Furthermore, the

pretreatment with Organosolv is implanted in a catalyst (a salt, an acid or a base) with temperatures below 200 °C; although, it generally depends on the type of biomass that is being pretreated [47]. There are many catalysts used in the literature, including acid, sodium hydroxide, and magnesium sulphate. Of all of them, sulfuric acid and sodium hydroxide have proven to be very effective in improving digestibility; whereas sulfuric acid is highly toxic and inhibitory in biogas production [63].

#### 3.3.4. Wet Oxidation

This treatment consists of applying oxygen to the manure with high temperature and pressure [64]. The temperatures necessary for pretreatment are around 140–200 °C with an approximate time of 30 min [65]. Wet oxidation makes the biomass susceptible to enzymatic hydrolysis, and pretreatment separates the raw material into cellulose, lignin, and hemicellulose fractions through its solubilization and degradation [12,66]. Wet oxidation is an alternative to steam explosion. Within chemical pretreatments, wet oxidation is more efficient to treat lignocellulosic materials, since the crystalline structure of cellulose opens during the process [67]. Organic molecules, including lignin, are broken down into CO<sub>2</sub>, H<sub>2</sub>O, and simpler and more oxidized organic compounds, mainly into low molecular weight carboxylic acids [68].

#### 3.3.5. Alkaline Peroxide

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) pretreatment is a low-cost pretreatment that results in increased accessibility of enzymes to the surface of the lignocellulosic material. Hydrogen peroxide removes and breaks the lignin walls that make up the biomass outer shell, making it more exposed to enzyme activity [69]. In this method, lignocelluloses are immersed in pH adjusted water (e.g., pH 11–12 with NaOH) containing H<sub>2</sub>O<sub>2</sub> at room temperature within 6 to 24 h period [12].

### 3.4. Biological Thermal Pretreatments

Currently, there are several biological pretreatments that are used to pretreat biomass and obtain higher biogas yields. However, all pretreatments employ microorganisms (white and soft rot fungi, actinomycetes, and bacteria) to degrade the recalcitrant material of lignocelluloses [70]. Biological pretreatment to improve biogas production in anaerobic digestion has mainly focused on fungus, microbial consortium pretreatment, and enzyme pretreatment [71].

White or brown rot fungi degrade lignin, and to a lesser extent cellulose and hemicellulose through a family of extracellular enzymes collectively called “lignases”, such as lignin peroxidase, manganese peroxidase, and laccase [72,73]. White rot fungi break down a broad spectrum of environmentally persistent xenobiotics and organic pollutants [74]. Thus, over a long period of time, biomass is inoculated with fungi lignolytic enzymes to degrade lignocellulosic material. Moreover, in biological pretreatment, several enzymes are required to achieve greater efficiency in biomass degradation. Mixtures of different enzymes cause greater synergy to expand small pores and increase access to the cell wall [46,75]. Although there is a diversity of fungi used in biological pretreatment, the most widely used are: *Phanerochaete chrysosporium*, *Trametes versicolor*, *Ceriporiopsis subvermispora*, *Pleurotus ostreatus*, *Ceriporia lacerata*, *Pycnoporus cinnabarinus*, *Cyathus cinnabarinus*, *Bjerkandera adusta*, *Ganoderma versceumum*, *Irpex lacteus*, *Lepista nuda* and *Phanerochaete chrysosporium*, *Sporotrichum*, *Aspergillus*, *Fusarium*, *Penicillium*, etc. [12,47].

Biological pretreatment through a microbial consortium mainly attacks cellulose and hemicellulose. Generally, microbes are extracted from natural environments, such as decomposing straw and thermophilic landfills [76]. The biodegradation of cellulose and hemicellulose under these microbial consortiums has turned out to be a very efficient pretreatment for biotechnological application, since it avoids the problems of regulation by feedback and repression of metabolites posed by isolated strains [77]. Finally, biological pretreatment also uses enzymes with hydrolytic activity that include cellulase and hemicellulase [78]. Many studies suggest that the addition of enzymes used in the pretreatment of manure can improve the performance of anaerobic digestion systems [79].

In general, biological pretreatments are not as expensive; however, they are slow and require a large space with fairly controlled environments to make their application more efficient [80]. Furthermore, for biological pretreatments to be feasible in the application of commercial biogas production, additional research is needed to address some key issues such as cost, selectivity, and efficiency [71].

Table 2 summarizes the different types of pretreatments most used. Most of them affect all lignocellulosic material; however, some affect more a part than the rest of the lignocellulose composition. The main effects of pretreatments on cellulose, hemicellulose and lignin are presented.

**Table 2.** Types of pretreatments most used to improve biogas production.

Pretreatments	Effects on Lignocellulosic Structure			References
	Cellulose	Hemicellulose	Lignin	
Physical				
Milling	Reduces crystallinity			[42,47]
Extrusion	Decreases the degree of polymerization			[11]
Microwave irradiation	Increases substrate availability for enzymes			[42,49]
Physicochemicals				
Steam explosion		Greater solubilization	Solubilization Alteration of the structure	[53]
Plasma	Degrades it into glucose			[52,54]
CO <sub>2</sub> explosion	Break the structures	Break the structures		[56]
Liquid hot water (LHW)		Increased solubilization and depolymerization		
Ammonia Fiber Expansion (AFEX)		Degradation in oligomeric sugars Deacetylation		[47]
Chemical				
Alkaline hydrolysis		Solubilization of hemicellulose	Decompose, alter and breakdown of lignin	[58,59]
Acid hydrolysis		Solubilization of hemicellulose	Decompose, alter and breakdown of lignin	[60]
Organosolv process		Solubilization of hemicellulose	Lignin solubilization	[63]
Wet oxidation			Lignin solubilization	[12,66]
Alkaline peroxide			Altered lignin structure	[69]
Biological				



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Pretreatment with microbial consortia, fungi and enzymes	Degrade cellulose	Degrades hemicellulose	Degrades lignin	[46,75]
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#### 4. Application of Pretreatments to Livestock Waste

##### 4.1. Pretreatments Applied to Cow Manure

Cow manure has provided low methane yield results [81], since it is made of highly undegradable material inhibiting the biogas production process. However, cow manure is highly available and has many advantages due to its synergistic nature to balance pH, C/N ratio and nutrient content [2]. Table 3 shows some pretreatments used in the monodigestion of cow manure to accelerate the hydrolysis phase. Most of the pretreatments analyzed are carried out in batch reactors and using inoculum to start the AD process.

**Table 3.** Effects of the different pretreatments applied to cow manure.

<b>Pretreatment</b>	<b>Process</b>	<b>Inoculum</b>	<b>Initials Condition</b>	<b>CH<sub>4</sub> (mL/g VS)</b>	<b>Methane Enhancement (%)</b>	<b>References</b>
Biological	Incubation (7 days, 70 °C with B4 bacteria to degrade hemicellulose)	Digested manure from a thermophilic laboratory reactor	V <sub>r</sub> = 0.117 L; TRH = 40–60 d; T = 55 °C	300.0	30	[82]
Physiochemical	125 °C, 37.5 min and 24 h	Digestate from a wastewater plant	TS = 16.12%; VS = 13.64%; pH= 7.85; C/N = 16.1; V <sub>r</sub> = 2 L; TRH = 40 d	450.0	35	[83]
Physiochemical	Boiler 11 (170 °C at 1 h)	-	TS = 34.66%; VS= 19.52%; pH= 8.57; V <sub>r</sub> = 0.250 L; TRH = d; T = 37 °C	130.2	-7	[84]
Physiochemical	68 °C (36, 108 and 168 h)	Digested sludge from cattle manure of a laboratory scale digester	V <sub>r</sub> = 116 L; TRH=70 d; T = 68–55 °C	260.0	56	[3]
Physical	Maceration with a blender <0.35 mm and pressurizing the manure to 100 atm	Digested manure from a thermophilic laboratory reactor	V <sub>r</sub> = 0.117; TRH = 40–60d; T = 55 °C	276.0	20	[82]
Physical	Mobile hammer mills. Sieving	Sludge from an anaerobic digester from a WWTP	TS = 19.6%; VS = 17.32%; pH = 8.23; V <sub>r</sub> = 1 L; TRH = 39 d; T = 35 °C	316.3	15	[85]
Physical	Combination of three plates: aluminum, sandpaper and stainless steel	Sludge from an anaerobic digester from a WWTP	TS = 223.59 g/kg; VS = 191.87 g/kg; pH = 8.32; V <sub>r</sub> = 0.164 L, TRH = 30 d; T = 53 °C	168.0	-	[4]
Chemical	Ca(OH) <sub>2</sub> , 60 °C, 12 and pH of 12	Sludge from an anaerobic digester from a WWTP	V <sub>r</sub> = 0.118 L; TRH = 45 d; T = 37 °C	225.0	76	[86]

Chemical	Calcium oxide (CaO)	Sludge from an anaerobic digester from a WWTP; sludge from an agroindustrial cow manure digester	TS = 9.84%; VS = 8.34%; pH = 7.15; Vr = 1.6 L; T = 38 °C	168.2	26	[87]
Chemical	Peracetic Acid (C <sub>2</sub> H <sub>4</sub> O <sub>3</sub> )	Sludge from an anaerobic digester from a WWTP; sludge from an agroindustrial cow manure digester	TS = 9.84%; VS = 8.34%; pH = 7.15; Vr = 1.6 L; TRH = 43 d T = 38 °C	182.4	39	[87]
Chemical and Physiochemical	NaOH 6% <i>p/p</i> TS 121 °C, 20 min	Sludge from a WWTP anaerobic digester	TS = 223.59 g/kg; VS = 191.87 g/kg; pH = 8.32; Vr = 0.164 L; T = 53 °C	168.0	155	[4]

\* In all tests a batch reactor was experimented. Vr is the volume of the reactor and THR is hydraulic retention time

Angelidaki and Ahring [82] conducted a study on biological pretreatment through B4 bacteria to degrade hemicellulose from cow manure. Digested manure from a laboratory reactor under thermophilic conditions was used as inoculum. Results showed that monodigestion can improve methane production by 30%, which implies a methane production of 300 mL CH<sub>4</sub>/g VS. However, not many studies have been conducted on the anaerobic biodegradability of monodigestion from cow manure with biological pretreatments.

In another study, Ferreira et al. [88] pretreated cow manure through a physicochemical (thermal) pretreatment. In this experiment the sample was pretreated at 125 °C. The results were positive, obtaining 450 mL CH<sub>4</sub>/g VS; that is, 35% more than the control tests. Similarly, Qiao et al. [84] carried out a study with cow manure, pretreating it in boilers at 170 °C. The results were not so favorable (130.2 mL CH<sub>4</sub>/g VS), which meant a decrease of 7% compared to the untreated material. The fact that methane production was low may be because no inoculum was used. Nielsen et al. [3] also used heat to pretreat cow manure. They carried out an experiment at 68 °C, using digestion of cow manure sludge from a laboratory scale digester as inoculum. They concluded that methane production can improve up to 56%. However, the accumulated methane production was 260 mL CH<sub>4</sub>/g VS.

As a physical pretreatment, Angelidaki and Ahring [82] mechanically pretreated cow manure. They macerated the manure to decrease the particle size to 0.35 mm, pressurizing it to 100 atm. In the test they used digested manure as the inoculum and obtained a methane production of 276 mL CH<sub>4</sub>/g VS. Through this pretreatment, methane production increased by 20%. In another experiment by Coarita et al. [85], they also pretreated cow manure under mechanical techniques. They used mobile hammer mills to grind the manure and decrease its size. They wet-sieved the samples at different particle size calibrations (0.25–31.5 mm). During the digestion process, they used sludge from an anaerobic digester of a treatment plant as inoculum and obtained productions of 316 mL CH<sub>4</sub>/g VS with improvements of 15%. Similarly, Tsapekos et al. [4] carried out studies on mechanical pretreatments with cow manure. They used a combination of three plates: aluminum, sandpaper, and stainless steel. The combination of these plates allowed them to apply shear forces on the samples and decrease the size of the manure. As in the previous case, they used anaerobic sludge from a sewage digester as inoculum. As a result of the pretreatment, they obtained a methane production of 168 mL CH<sub>4</sub>/g VS. Mechanical pretreatment showed a positive effect on the digestibility of the fibers, which caused a four-fold production improvement.

Another type of pretreatment that has been widely used in the literature is the chemical pretreatment, using either alkaline or acidic compounds [89]. For one thing, alkaline pretreatment involves the use of bases such as sodium, potassium, calcium and ammonium hydroxide, for the pretreatment of livestock manure [11]. Generally, the accessibility to carbohydrates of lignocellulosic biomass is limited, but can be improved with alkaline pretreatment [90]. Seyedy et al. [86] in an experimental study showed the possibility of improving biogas production from cow dung with Ca(OH)<sub>2</sub> lime as a pretreatment. Their studies contain the pretreatment of cow manure in different alkaline conditions at a pH of 12 for 12 h. The alkaline pretreatment results achieved a 76% improvement in methane production with respect to the untreated material; this was 225 mL of mL CH<sub>4</sub>/g VS. Seyedy et al. [88] used calcium oxide (CaO) to pretreat cow manure. They showed that its monodigestion markedly improves methane production by up to 26%. They used sewage sludge mixed with sludge from an agroindustrial cow manure digester to optimize the process, obtaining 168.2 mL CH<sub>4</sub>/g VS of methane. Similarly, Ramos et al. [87] considered that the optimal conditions for alkaline pretreatment are based on using sodium hydroxide (NaOH) at a concentration of 6% *p/p* of total solids with a temperature of 121 °C for 20 min. During co-digestion, they used sewage sludge and managed to obtain 168 mL CH<sub>4</sub>/g VS of methane, which represents an increase of 155% compared to the untreated samples. Another way to apply chemical pretreatment is through acidic compounds, since it has a high selectivity with lignin [91]. A commonly used chemical compound is peracetic acid (PAA) as it solubilizes lignin by cleaving bonds resulting in lignin cleavage [92]. Ramos et al. [90] used peracetic acid (PAA) to improve methane production from cow manure. They carried out an experiment where they used as an inoculum mud from an anaerobic digester of a waste water

treatment plant (WWTP). They obtained 182.4 mL CH<sub>4</sub>/g VS, which meant a 39% improvement in methane production with respect to the untreated material.

Overall, studies show that pretreatments solubilize cow manure by increasing biodegradability and methane production. The most widely used treatments combine more than one pretreatment, as is the case of physicochemical by the addition of heat. In regard to chemical pretreatments, alkali compounds of NaOH and Ca(OH)<sub>2</sub> are commonly used. While temperature improves the production of biogas, temperature above 200 °C inhibits the fermentation process, decreasing biogas production.

#### *4.2. Pretreatments Applied to Pig Manure*

Pig manure as raw material has great potential in production of biogas. However, it requires methods to optimize its biodegradation process and eliminate difficult-to-decompose materials impeding the hydrolysis acceleration process. Table 4 shows some pretreatments used to improve the biogas production of AD from this raw material. In a study on anaerobic digestion, Qiao et al. [84] evaluated the biogas production from pig manure residues with and without hydrothermal pretreatment. The pretreatment was carried out in eight stainless boilers applying 170 °C for one hour. The researchers obtained a methane productivity of 290.8 mL CH<sub>4</sub>/g VS, resulting in a 14.6% increase. Ferreira et al. [88] applied a thermal pretreatment to a pig manure mixture by means of a thermal steam explosion. They evaluated the methane yield of the separated solid fraction of pig manure under different combinations of temperature and duration. They determined that the optimal temperature–time combinations of the pretreatment were 170 °C and 30 min. They managed to double the methane production from 159 to 329 mL of CH<sub>4</sub>/g VS, which represented an improvement of 206.9%. They demonstrated that temperature has a greater effect on methane yield than pretreatment time. Rafique et al. [93] used heat pretreatment on dehydrated pig manure. They demonstrated that the maximum amount of biogas is obtained when the substrates were pretreated with temperatures of 100 °C; however, above this temperature, production decreased rapidly. During monodigestion, they used sludge from an anaerobic digester from a WWTP as inoculum. After pretreatment, they obtained 25% improvements, with a production of 237.5 mL of CH<sub>4</sub>/g VS.

**Table 4.** Effects of the different pretreatments applied to pig manure.

Pretreatment	Process	Feedstock	Inoculum	Initials Condition	CH <sub>4</sub> (mL/g VS)	Methane Enhancement (%)	References
Physiochemical	170 °C at 1 h	Pig manure	-	TS = 28.14%; VS = 22.26%; pH = 6.91; Vr = 0.250 L; TRH = 43 d; T = 37 °C	290.8	14.6	[84]
Physiochemical	Thermal steam explosion (170 °C and 30 min)	Pig manure	Sludge from a WWTP anaerobic digester	TS = 46.6 g/kg; VS = 36.8 g/kg; C/N = 8.5; Vr = 0.300 L; T = 35.1 °C	329	206.9	[88]
Physiochemical	(100 °C) 1h	Dehydrated pig manure	Sludge from an anaerobic digester from a WWTP	TS = 46.6 g/kg; VS = 36.8 g/kg; C/N = 8.5; Vr = 0.300 L; TRH = 29 d; T = 35.1 °C	237.5	28	[93]
Chemical	Ca (OH) <sub>2</sub> at 5%, 2 h and neutralization of pH with HCl	Dehydrated pig manure	Sludge from an anaerobic digester from a WWTP	TS = 46.6 g/kg; VS = 36.8 g/kg; C/N = 8.5; Vr = 0.300 L; TRH = 29 d; T = 35.1 °C	204.74	12	[93]
Chemical	6% NaOH (p/p)	Pig manure	Anaerobic sludge from a beer plant	TS = 84.5%; VS = 67.76%; Vr = 0.500 L; T = 35 °C	232.4	21.4	[29]
Chemical	Ca(OH) <sub>2</sub> , 1 h (70 °C)	Dehydrated pig manure	Sludge from an anaerobic digester from a WWTP	TS = 46.6 g/kg; VS = 36.8 g/kg; C/N = 8.5; Vr = 0.300 L; TRH = 29 d; T = 35.1 °C	345	72	[93]
Biological	Microbial community cell biocatalyst to accelerate degradation of antibiotics	Pig manure	-	TS = 28.14 %; VS = 22.26 %; pH = 6.91; Vr = 0.420 L; TRH = 7 d	98.7	93.2	[94]

Physical	Liquid and solid matrix separation using a 0.25mm pore size screen	Pig waste slurry	Sludge from an anaerobic digester from a WWTP	TS = 11.4%; VS = 9.34%; Vr = 1 L; TRH = 30 d; T=32 °C	251 mL/g DQO	-2.33	[95]
Physiochemical	Power at 600 W. The temperature increased with a ramp of 10 °C/min until reaching 80 °C and was maintained for 15 min supplemented with C	Pig manure	Sludge from an anaerobic digester from a WWTP	TS = 23.1g/l; VS = 15.2g/L; pH = 6.9 C/N = 10.9; Vr = 0.250 L; TRH = 30 d; T = 35 °C	433.2	39	[96]

\* In all tests a batch reactor was experimented. Vr is the volume of the reactor

Another class of pretreatments that are useful for improving methane production from pig manure are chemical pretreatments. The use of compounds such as NaOH are highly efficient in improving pig manure fermentation through the solubilization of hemicellulose [97]. Zhang et al. [29] used NaOH with a concentration of 6% based on the total solids of the sample. After pretreatment, the content of lignin, cellulose and hemicellulose decreased from the respective values of 18.36%, 32.36%, and 14.6% to 17.10%, 30.07%, and 10.65%. During the digestion process, they used anaerobic sludge from a beer plant as an inoculum, which reduced the amount of TS and VS by 48.5% and 70.4%, respectively. With the application of this pretreatment, they obtained a methane production of 232.4 mL of CH<sub>4</sub>/g VS, which meant an improvement of 21.4% compared to the untreated materials. Meanwhile, Rafique et al. [93] used a chemical pretreatment on pig manure, focused on alkaline compounds. The samples were pretreated with Ca(OH)<sub>2</sub> with a concentration of 5% for 2h; furthermore, before starting the AD process, they added hydrochloric acid (HCl) to the pig manure digesters to neutralize their pH. In the fermentation process, as inoculum, they used sewage sludge in mesophilic conditions for 29 days. At the end of the digestion time, they obtained a production of 204.74 mL of CH<sub>4</sub>/g VS with an improvement of 12% compared to the controls. Furthermore, under the same conditions as above, they carried out another test using Ca(OH)<sub>2</sub> as a pretreatment for pig manure, but applying a temperature of 70 °C. In this case, methane production was remarkably increased, reaching 345 mL CH<sub>4</sub>/g VS, meaning a 72% increase. They showed that the use of temperatures not higher than 70 °C during the alkaline pretreatment optimizes the methane production.

Another type of pretreatment that improves methane production is biological. According to Feng et al. [98], many of the antibiotics administered to pigs are usually released through their droppings. In this sense, Liu et al. [94] carried out a study to eliminate β-lactam antibiotics present in pig manure in a biological way. They demonstrated that removing antibiotics from pig manure can greatly improve methane production. They carried out the biological pretreatment using a biocatalyst made up of a microbial community that accelerates antibiotics degradation. With pretreatment, penicillin, cefamezine, and amoxicillin were completely degraded by the biocatalyst for 1h. Pretreatment increased methane production by 93.2% when pretreatment was performed for 3 days.

To further improve the anaerobic biodegradability of pig manure, there are pretreatments that have emphasized mechanical pretreatment through sample screening. González et al. [95] designed an experiment to improve methane production through liquid and solid separation of pig manure. The particles were separated from the samples using a 0.25 mm pore size screen. However, the application of this method was not very successful in improving methane. Production decreased to 251 mL/g COD, which meant a 2.33% decrease compared to the controls. Another widely used technique is the pretreatment by microwave irradiation, as carried out by Gómez et al. [96]. The test was carried out by setting a power of 600 W (maximum efficiency of 80%). The temperature was increased with an interval of 10 °C/min until reaching 80 °C and they kept it that way for 15 min. At the end of the digestion process, they obtained a methane production of 433.2 mL CH<sub>4</sub>/g VS, improving production by 39% compared to the tests without pretreatment.

To sum up, pig manure physical pretreatments by milling and extrusion did not exactly improve methane production; however, microwave irradiation had more effect on improving substrate biodegradability. On the other hand, there are a few biological pretreatment studies that focus on increasing pig manure production. For that matter, the application of thermal and alkaline pretreatment enhances anaerobic digestion, significantly yielding higher biogas and methane. Alkaline heat pretreatments were proven more effective than acid pretreatments in pig manure hydrolysis.

#### 4.3. Pretreatments Applied to Poultry Manure

It has been demonstrated that through different methods and pretreatments, the lignocellulosic content of poultry manure can be decreased to accelerate the hydrolysis phase and improve the accumulated production of methane [11]. In this regard, increasing attention has been paid to the use of poultry manure, especially chicken litter, as an alternative source for bioenergy production [99].



Table 5 shows some pretreatments aimed at improving biogas production from poultry manure. Costa et al. [100] studied the pretreatment of sand for birds and chicken feathers with NaOH and  $\text{Ca}(\text{OH})_2$  at different temperatures and pressures. They carried out the pretreatments applying the following conditions:  $\text{Ca}(\text{OH})_2$  at 90 °C with 1 bar pressure;  $\text{Ca}(\text{OH})_2$  at 90 °C and 1.27 bar pressure, and with NaOH at 90 °C and 1.27 bar pressure. They demonstrated that the best treatment was to pretreat the manure with  $\text{Ca}(\text{OH})_2$  at 90 °C and 1.27 bar pressure for 120 min. The anaerobic digestion process was carried out under mesophilic conditions (37 °C) with anaerobic sludge from a wastewater treatment plant used as the inoculum, obtaining 137 mL  $\text{CH}_4/\text{g VS}$ . Zahan and Othman [101] also conducted studies with chicken litter under alkaline conditions and using an alkaline–acid sequence. For alkaline conditions, they pretreated the samples with 5% NaOH at 120 °C for 90 min, while for alkaline–acid conditions, they used 5% NaOH at 120 °C for 90 min and 3%  $\text{H}_2\text{SO}_4$  at 120 °C for 90 min. They demonstrated that alkaline pretreatment was the most appropriate and the one that provided the best results. After the anaerobic digestion process was completed, they obtained 481.5 ml  $\text{CH}_4/\text{g VS}$ , which represented an improvement of 50% compared to untreated testing.

**Table 5.** Effects of the different pretreatments applied to poultry manure.

Pre-treatment	Process	Feedstock	Inoculum	Initials Condition	CH <sub>4</sub> (mL/g VS)	Methane Enhancement (%)	References
Chemical	5% de NaOH 90 min 120 °C + 3% de H <sub>2</sub> SO <sub>4</sub> 90 min 120 °C	Chicken litter	Sludge from an anaerobic digester from a WWTP	TS = 77.2%; VS = 39.1%; pH = 8.15; C/N = 13.02; V <sub>r</sub> = 1 L; T = 37 °C	481.5	50	[101]
Chemical	Ca(OH) <sub>2</sub> at 90 °C y 1.27 bar pressure	Chicken litter and chicken feathers	Anaerobic sludge from a wastewater treatment plant	TRH = 80 d; T = 37 °C	137	-	[100]
Biological	<i>Clostridium cellulolyticum</i> , <i>Clostridium saccharolyticum</i> and <i>Clostridium thermocellum</i> as bioaccumulation strains	Poultry manure	Sludge from an anaerobic digester from a WWTP	TS = 77%; VS = 70%; V <sub>r</sub> = 0.05 L; T = 37 °C	102	15%	[100]
Biological	2–8 days at total solid concentrations of 5–20% by <i>Bacillus sp. C4</i>	chicken feathers	Sludge from an anaerobic digester from a WWTP	TS = 92.05 %; VS = 89.78%; C/N = 3.66; V <sub>r</sub> = 0.056 L; TRH = 55 d; T = 37 °C	430	292	[102]
Thermal	Pressure in a stirred tank 150 °C/5 min and 4.8 bar	Poultry manure	Digestate from a biogas plant from cattle manure and corn silage	TS = 52.73 %; VS = 37.25%; V <sub>r</sub> = 0.05 L; T = 39 °C	288	14.4	[103]
Physiochemical	(70 °C) from chicken manure under 3-day HRT	Poultry manure	Sludge from an anaerobic chicken manure reactor Anaerobic sludge from anaerobic digester from cow, corn and grass manure	Reactor CSTR; V <sub>r</sub> = 16 L; TRH = 120 d; T = 55 °C	518	54.6	[104]
Physiochemical	High pressure and temperature reactor (T = 200 °C, 15 min)	Poultry manure		V <sub>r</sub> = 0.500 L; TRH = 90 d; T = 35 °C	340	-7.86	[105]

\* In all tests a batch reactor was experimented. V<sub>r</sub> is the volume of the reactor

On the other hand, many investigations focus on biological pretreatment methods, which are sustainable, ecological and profitable to extract soluble keratins through the use of microorganisms [102]. Patinvoh et al. [106] used strains of bacteria (*Bacillus sp.C4*) to pretreat chicken feathers and produce biogas. The samples were pretreated for 2 to 8 days with concentrations of 5–20% of the total solids. They performed anaerobic digestion, using sludge from a wastewater treatment plant as inoculum and obtained improvements of 292%, producing 430 mL CH<sub>4</sub>/g VS. In another study, Costa et al. [100] performed the biological pretreatment of organic poultry manure with *Clostridium cellulolyticum*, *Caldicellulosiruptor saccharolyticum* and *Clostridium thermocellum* as bioaccumulation strains. They used sewage sludge from a treatment plant as inoculum in the anaerobic digestion process. They concluded that biologically pretreated manure allows methane productions of 102 mL CH<sub>4</sub>/g VS to be obtained, which means an improvement of 15% compared to untreated manure

Hydrolysis continues to be the limiting step in the fermentation process since it prevents optimal degradation of the lignocellulosic material. Furthermore, the accumulation of nitrogen and ammonia in the manure of the birds prevents efficient conversion of bioenergy [107]. For its part, chicken manure contains materials that produce alkalinity and ammonia accumulation, that is, proteins and uric acid [108]. Therefore, a technology that reduces the negative effects caused by the accumulation of ammonia in the anaerobic system is necessary to optimize the production of biogas. Yin et al. [104] launched a device to extract ammonia in the gas phase. They extracted ammonia from poultry manure by exposing the samples to 70 °C for 3 days. The fermentation was carried out, using sludge from an anaerobic chicken manure reactor and in a continuous stirred tank reactor (CSTR) as inoculum. At the end of the digestion process, they concluded that after applying the hyperthermophilic pretreatment to the manure, it was possible to obtain a methane production of 518 mL CH<sub>4</sub>/g VS, which represented an improvement of 54.6% compared to controls.

Although some studies have been conducted on the effect of high temperatures on chicken manure, few have focused on a wide range of temperatures, particularly temperatures of 200 °C and above. In this way, Raju et al. [105] pretreated chicken manure under isochoric conditions for 15 min at temperatures between 100 and 225 °C with intervals of 25 °C. After 27 days of incubation, in batch reactors, the methane production was 340 mL CH<sub>4</sub>/g VS at 225 °C, which meant a decrease of 7.86%. Nevertheless, there were no significant changes at lower temperature compared unpretreated samples. Consequently, this pretreatment process is considered unsuitable for this type of manure.

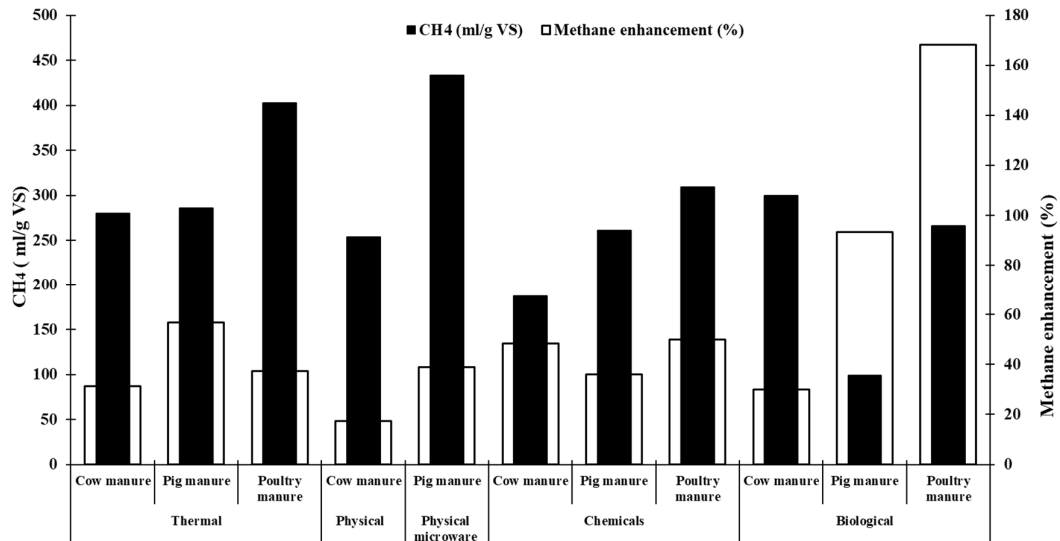
Out of all studies carried out, the thermochemical poultry manure pretreatment has the most effective results regarding biogas and methane production. In addition, alkaline treatments with the use of NaOH and Ca(OH)<sub>2</sub>, with the addition of heat, are the most widely used and are the ones that significantly improve the hydrolysis of poultry manure. For their part, biological pretreatments have played a leading role in increasing production; up to 292% improvements have been obtained using fungi and enzymes. On the other hand, it was discovered that the pretreatment isochoric conditions does not improve the yield; on the contrary, they decreased the amount of methane by up to 8%.

## 5. Summary of the Effects of Pretreatment on Animal Manure

### 5.1. Comparison of the Main Pretreatments

The physical, physicochemical, chemical and biological pretreatments used in the literature are variable in their application, which means that each one has its own singularities: type of concentration, application times, temperature, etc. Furthermore, in the anaerobic digestion process, the researchers use various operating parameters (hydraulic retention time, digestion temperature, VS concentration, agitation, pH and C/N ratio). Many operating parameters, individually or together, are decisive; their choice is conditioned by their suitability and flexibility [109]. On the other hand, the characteristics of the elemental and proximal analysis of the raw material (animal manure) are not the same in each of the investigations consulted; there is a lot of variability between them, although the same type of substrate is analyzed. In this sense, making a comparison between the pretreatment methods is complex since it depends on various conditions and factors.

In Figure 2, a comparison is made between the different types of pretreatments obtained in Tables 3–5; a rough quantitative assessment of its impact on methane production is shown. The figure shows the average methane production in cow, pig and poultry manure after applying a pretreatment. Furthermore, the improvement in methane production between pretreated and untreated raw materials is estimated.



**Figure 2.** Methane production from cow, pig and poultry manure with respect to physical, chemical, thermal and biological pretreatments.

Thermal and hydrothermal pretreatments provide the most methane. They include production ranges between 130 to 450 mL/g VS for cow manure, 238 to 329 mL/g VS for pig manure and between 288 to 518 mL/g VS for poultry. They were more effective for pig manure with improvements of 12 and 206.9%. For their part, mechanical pretreatments (microwave irradiation) have had more effect on pig manure with 433 mL/g VS and improvements of 39%. On the other hand, mechanical pretreatments such as milling and extrusion have been used more in the pretreatment of cow manure, obtaining methane productions from 168 to 316 mL/g VS with improvements of 15 to 20%. On the other hand, chemical pretreatments have been the most widely used in the literature, especially alkaline chemicals. Its influence on cow manure has resulted in methane productions of 168 to 225 mL/g VS, with improvements of 26 to 155%. Instead, its effect on pig manure is 205 to 345 mL/g VS with improvements of 12 to 72%. In poultry manure, more effective results were observed with values of 137 to 482 mL/g VS and improvements of 50%. Finally, biological pretreatments also have positive effects on the pretreatment of animal manure, although their use has been less frequent. Thus, in cow manure, methane productions of 300 mL/g VS and improvements of 30% have been obtained. In pig manure its effect has resulted in methane productions of 99 mL/g VS. In poultry, they have been very effective, as methane productions of 102–430 have been obtained with improvements of 15 to 292%.

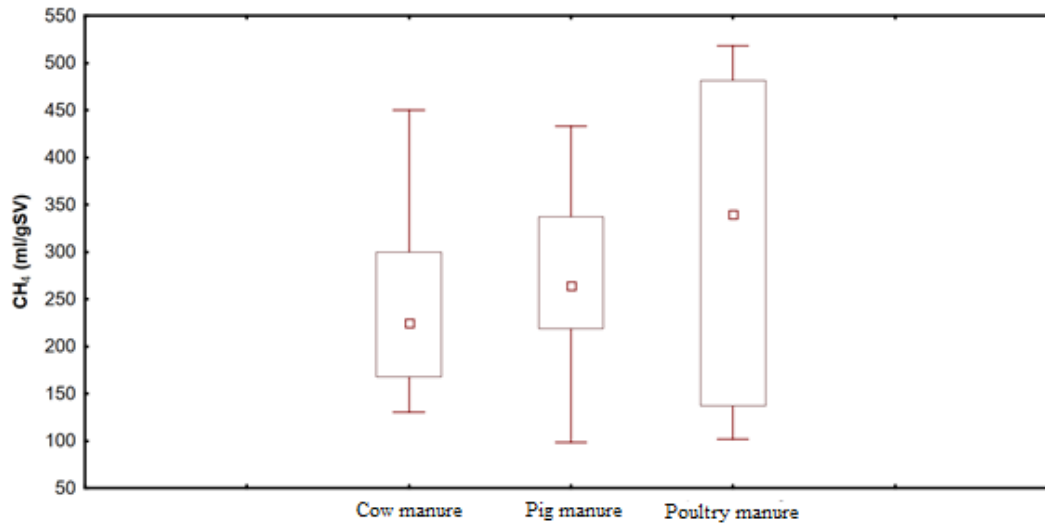
Biological pretreatments are those that best optimized the AD of the different types of animal manure, that is, they improved methane production by 74%. Its most effective application was in poultry manure since improvements of 168% were obtained in this raw material. In contrast, chemical pretreatments experienced improvements of 45%; they had more effect on cow and poultry manure with improvements of 48% and 50%, respectively. Third, thermal pretreatments registered improvements of 41%; they were more effective in treating pig and poultry manure, as they improved production by 57% and 37%, respectively. Finally, the application of physical pretreatments had less effect on animal manure. These pretreatments improved AD by 30%; however, they were more effective in pig manure, as they improved their production by 39%.

Methane productions, expressed in mL CH<sub>4</sub>/g VS, are the average of the data collected in Tables 3–5. In each type of pretreatment, the average methane production in each of the cow, pig and poultry

manure residues has been calculated. <sup>2</sup> The improvement in methane production, expressed in %, has been estimated from the methane productions in Tables 3–5. The improvement has been obtained by relating the methane averages of the untreated substrates with the pretreated averages.

### 5.2. Effect of Pretreatments on Cow, Pig and Poultry Manure

As in the previous case, this section analyzes the methane results obtained in Tables 3–5 after applying the different types of pretreatment. Figure 3 shows the influence of pretreatments on animal manure waste. It is analyzed in which type of manure (cow, pig and poultry) its methane production increases more easily.



**Figure 3.** Box of whiskers from the production of pretreated methane from cow, pig and poultry manure.

In general, the VS concentration of animal manure from the analyzed data is not so high, which means that the average ranges for the production of pretreated methane from cow, pig and poultry manure are 238, 271 and 328 mL/g VS, respectively. According to Velázquez et al. [110], substrates with low, medium and high methane production are characterized by having productions between 150 and 300 mL/g VS, between 300 and 400 mL/g VS, and more than 450 mL/g VS, respectively. In this research, the average methane production of cow and pig manure corresponds to a low production, while the methane production of poultry corresponds to an average production.

The analyzed data collected in this study show that the application of pretreatments to cow manure improves the average yield of biogas and methane compared to untreated manure. Improvements for all registered pretreatments ranged from 15 to 155%. Regarding pig manure, this had improvements between 12 and 206.9%. On the other hand, the behavior of the pretreatments with respect to the manure and feather of poultry made it improve the production of methane. In this case, the improvements ranged between 14 and 292%. In general, animal manure is suitable to produce biogas. However, it should be borne in mind that the results of a pretreatment is not always appropriate for any anaerobic digestion process [11]. No pretreatment method is suitable for all anaerobic digestion processes and substrates; each pretreatment has its own advantages and disadvantages [111]. The different pretreatment technologies described above may be more suitable for a particular reactor design or size [112]. Thus, efforts to optimize the fermentation process should be aimed at finding the appropriate substrate composition and, at the same time, adequately characterizing the substrate so that its bioavailability can be increased through pretreatment. This is because the lignocellulosic composition of each manure is very particular, which means that not all pretreatments are adequate to accelerate its degradability process.

The box of whiskers was estimated from the results of Tables 3–5. The methane estimates from cow, pig and poultry manure include all pretreatments (physical, physicochemical, chemical and biological).

## 6. Perspectives and Challenges of Animal Manure Pretreatments

This document has reviewed the available pretreatment methods for animal manure waste as a substrate prior to the AD process. It is highlighted that pretreatments are a necessary process, and that they can significantly improve methane production. However, most pretreatments lose their effectiveness due to the lignin content present in the waste. Thus, in the degradation of lignin from cow, pig and poultry manure residues, the solubilization and depolymerization of lignocellulosic components are the main obstacle during AD [52].

Each of the analyzed technologies has its own associated advantages and disadvantages, depending on the biomass source, the methods used and the lignocellulosic composition [113]. The efficiency on the application of a pretreatment is highly related to the characterization of the substrate. Thus, the biggest challenge to pretreating substrates is to combine the ideal substrate composition with the most appropriate pretreatment technique. Thus, for example, in this study it is revealed that physical pretreatment methods have been used more frequently to treat cow manure. This is because physical pretreatments are used in large-scale applications and one of their drawbacks is high energy demand and high maintenance costs [20]. While physicochemical pretreatments are applied to all types of manure analyzed, its efficacy is more closely related to the temperature and duration of the pretreatment. However, the application of a physicochemical (thermal) pretreatment generates higher methane production in poultry manure. As regards chemical pretreatments, the most widely used are alkalis, mainly because they more easily degrade the lignin content. The decision to use this type of pretreatment will depend on the cost of the chemicals and the ability to control the inhibition of some compounds. Finally, biological pretreatments provide environmental benefits and are profitable due to their low energy demand. However, the information in the literature shows that its application in pig manure has been little studied. One of the challenges is defining the correct enzyme set, since the composition of carbohydrates, lipids and proteins, as well as the lignin content, can be extremely variable in substrates [114].

The challenges of evaluating the effect of pretreatment on improving AD have a huge gap between laboratory results and those of a pilot and industrial scale; most of the literature studies have been conducted on a small scale.

To date, the pretreatment of livestock residues for biogas production has not been as widely studied as other organic substrates. In general, few pretreatment methods have been explored, most of them only in Biochemical Methane Potential tests in laboratory.

Studies on the optimization of pretreatments are focused on the solubilization of biomass and the increase in methane production. All these efforts have been very useful and interesting; however, the mechanisms that affect the complete solubilization of the cell wall structure are still not well understood.

Many studies collected from the literature lack an economic and environmental approach, which limits the most efficient proportion of results regarding the bioconversion of livestock residues to biofuel.

The evaluation of pretreatments to improve performance could be optimized with the combination of several pretreatments. The current literature on animal manure includes few studies in this regard; the combinations found are based solely on the contribution of heat to chemical pretreatments.

## 7. Conclusions

The main pretreatments (physical, chemical, physicochemical and biological) have the potential to increase enzyme accessibility by improving the susceptibility of animal manure to hydrolysis and subsequent anaerobic digestion. However, each technology has its own associated advantages and disadvantages, depending on the biomass source and the methods used.

In livestock waste treatments (cow, pig and poultry manure), biological pretreatments improved methane production by 74%, chemical pretreatments by 45%, thermal pretreatments by 41% and physical pretreatments by 30%.

The main bottleneck that prevents improving methane production from livestock waste is the lignin content, as it creates protective barriers that prevent microbial action and the development of hydrolysis. However, pretreatment of the waste before anaerobic digestion significantly improves methane production.

Pretreated methane production for cow manure was 238 mL/g SV, for pig manure 271 mL/g SV and for poultry manure 328 mL/g SV; with improvements of 32%, 45% and 46%, respectively.

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