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Research Article

ASSESSMENT OF THE DISCHARGE CHARACTERISTICS FROM AYURVEDIC PHARMACEUTICAL INDUSTRIES AND POTENTIAL VALORIZATION

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ABSTRACT

Ayurvedic medicine-based pharmaceutical industries are among the most profitable worldwide. After extracting the active ingredients, the herbal pharmaceutical industries produce an appreciable amount of wastewater in addition to solid herbal wastes. The current study focuses on the thorough physico-chemical characterization of the wastewater and solid residue for parameters, including pH, TSS, TDS, COD, BOD, TKN, TP, Oil and Grease (O and G), etc. Based on the results, it is reasonable to conclude that wastewater characteristics, including pH, O and G, organic load, and nutrients, vary considerably among industries, and hence it would be difficult to define a precise range of wastewater parameters. The effluent from ayurvedic pharmaceuticals may be generally characterized as having an acidic nature, more O and G and less nutrients (TKN and TP). Additionally, the results of the Biochemical Methane Potential Test (BMP) were encouraging in terms of the capacity of wastewater to generate biogas. It was found that the different regulating parameters of anaerobic treatment, including pH, VFAs, alkalinity, and VFA/Alkalinity ratio, were within the range, indicating better process stability. The biomass compositional analysis showed that the residue was primarily lignocellulosic in origin, with cellulose, hemicellulose, and lignin contents ranging from 34% to 41%, 17% to 20%, and 31%-38%, respectively, for both herbal and oil residues. Since lignocellulosic biomass is difficult to decompose, it is preferable to dry the solid waste and utilize it as a solid fuel.

INTRODUCTION

Ayurveda, the ancient medical system of India, is one of the oldest and most vibrant cultures in the world (Chauhan, et al., 2015). In recent years, Ayurveda has evolved into a comprehensive therapeutic system in the form of ayurvedic services and products (Subrat, et al., 2002; Singh, et al., 2016). Rising awareness of the advantages of living a healthy lifestyle, expanding consumer demand for chemical-free natural products, and supportive government policies have all contributed to the expansion of the Ayurveda business in India. The Indian ayurveda market is expected to develop at a Compound Annual Growth Rate (CAGR) of 16.06 percent between 2019 and 2024, from Indian Rupees (INR) 300 billion in 2018 to INR 710.87 billion in 2024. Moreover, Asia will account for 79% of market growth throughout the projection period (Ministry of Ayush, 2018).

The country's current state of herbal pharmaceutical enterprises demonstrates that products are made in batches. The process of making medicines uses a variety of plant materials, including roots, stems, leaves, seeds, flowers, bark, and more (Jain et al., 2000). The parts of natural herbs are cleansed, and then chopped or ground to reduce particle size as needed and then subject to extraction fermentation, distillation, decoction, and percolation as required

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(Otavio, et al., 2011). After the active ingredients were extracted, the entire process produces a significant amount of effluent, together with the solid herbal wastes. It is, therefore, essential to manage such wastewaters and solid residues in a techno-economic and environmentally sustainable manner. In view of this, the major objectives of this study include a comprehensive physico-chemical and composition analysis of the wastewater and solid waste from the ayurvedic pharmaceutical industry, as well as an assessment of its biochemical methane potential for its valorization and sustainable management.

MATERIALS AND METHODS

Study Area

Three industries engaged in the manufacturing of ayurvedic pharmaceutical products were selected for this study. Industries 1 and 2 are situated in Thrissur, Kerala, and produce more than 200 products. Some of them include chyavanaprasa, saraswatharishtam, sivagulika, asthra, etc. Industry 3 is situated in Thiruvananthapuram, Kerala, and mainly produces traditional medicines such as lehiyum and thailam. Industry 1 and 2 produce wastewater to the tune of 10,000 L/day whereas, industry 3 can be considered as a cottage industry that produces nearly 100 to 200 Liters of wastewater after every batch of either Lehiyum or Thailam, mostly from cleaning of vessels.

Wastewater Collection and Analysis

From industry 1, a grab sample P1 of the raw effluent was collected from the equalization tank which has a Hydraulic Retention Time (HRT) of more than 8 Hrs. From industry 2, a total of five grab samples were collected such as raw juice (S1), pre-process (S2), post production (S3), process ongoing (S4) and mixed sample (S5). The activities that produces pre-process wastewater (S2) includes the water utilized before starting the batch for cleaning the floor with detergents and washing utensils, etc. The post production wastewater (S3) is wastewater produced after the batch mainly used for cleaning the utensils after medicines or products are prepared and emptied. The changing of the utensils to prepare additional medicines, which are washed and produce wastewater is termed process ongoing (S4). All four samples—juice, pre-process, post-production, and ongoing—are combined to form mixed samples (S5). From industry 3, the wastewater samples from the vessel washings of Lehiyum (S6) and Thailam (S7) production were collected. Lehiyum are thick syrup-like semisolid ayurvedic medications with a sweet taste made from sugar syrup, jaggery, herbal pulp, powder, decoctions, and other components. Ayurvedic Thailams are ayurvedic massage oils used in ayurvedic therapies. All the wastewater samples were kept at 4oC and analyzed for various physico-chemical parameters viz. pH, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Volatile Suspended Solids (VSS), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Oil and Grease (O and G), Total Kjeldahl Nitrogen (TKN), Total Phosphorus (TP), etc. as per the procedure mentioned in standard methods (APHA, 2015).

Biochemical Methane Potential (BMP)

The Biochemical Methane Potential (BMP) test was done for P1, S5, S6 and S7. The experimental set-up is shown in Fig 1. And all the experiments for each of the samples were carried out in duplicates. Briefly, the ratio of COD of substrate to that of inoculum was maintained at 0.5 in the digestion bottle. The gas generated from the process was measured using the water displacement method. The test was run for 20 days and the gas generation was measured daily. The governing parameters such as pH, VFAs and alkalinity were measured on 0th, 6th, 12th and 20th day. The VFA and alkalinity measurements were done as per (Anderson and Yang, 1992). Additionally, the change in COD concentration of the mixture (inoculum+substrate) was measured on 0th, 5th, 10th and 20th day.

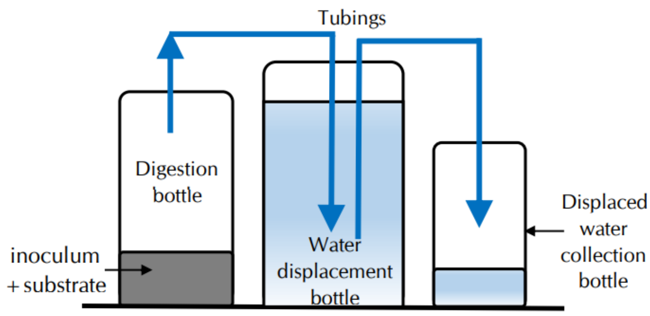

Fig. 1 Experimental set-up for Biochemical Methane Potential (BMP) test.

Collection of Solid Residue and Characterization

Raw biomass materials were solid and oil residue from Industry 1 and Industry 3 after as shown in Fig 2. No solid residue could be collected from industry 2. The solid residues are simple the leftover of plant materials after extraction of juices. The oil residue is formed when plant materials are boiled along with the oil while preparing thailam.

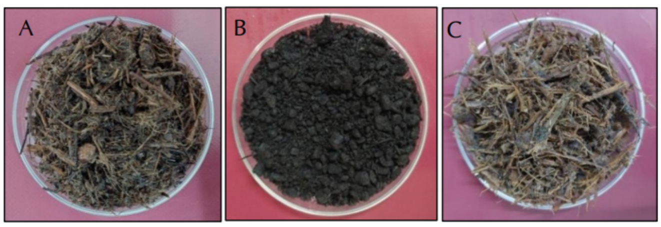

Fig. 2 A. Industry 1 solid residue B. Industry 3 solid+oil residue while preparing thailam C. industry 3 solid residue.

The useful phytochemicals then leach out in the oil solution. After the end of the batch, the plant materials are then separated from the oil solution and squeezed to further remove the phytochemicals. Each of the residues was analyzed for moisture content, Fixed Solids (FS), and Volatile Solids (VS). Additionally, the compositional analysis of all the solid residues was done using National Renewable Energy Laboratory (NREL) method (TAPPI method number T264) for the assessment of lignin, cellulose, and hemicellulose.

RESULTS AND DISCUSSION

Physico-Chemical Characteristics of Ayurvedic Pharmaceutical Wastewater

The characteristics of the wastewater samples collected are presented in Table 1. In general, all the effluent samples were turbid, greasy, and slightly greenish in color. All the wastewater samples except S7 were found to be acidic in nature with their pH ranging from 2.9 to 6.8. Sample S1 was the freshly extracted juice from herbs/ plants that showed the lowest pH i.e. 2.9. The characteristics of wastewater from industry 1 are quite weak in terms of COD, BOD, and TSS due to the mixed nature of the sample and on of collection, there wasn't much production.

From the available data, it was found that BOD ranged from 466 mg/L to 85000 mg/L and the corresponding Chemical Oxygen Demand (COD) ranged from 750 mg/L to 166696 mg/L. It was found that the BOD5/COD ratio ranged from 0.3 to 0.6. The BOD/COD ratio reflects wastewater biodegradability; the higher the ratio, the higher the biodegradability of the effluent (Papadopoulos, et al., 2001). The ratio of BOD to COD for Ayurveda pharmaceutical wastewater has been found in the range of 0.3-0.60, which shows the biodegradable nature of the wastewater (Stoddard, et al., 2002).

The one thing that was common in all the wastewater samples was the less concentration of nutrients such as nitrogen (measured as TKN) and phosphorus (measured as TP).Carbon, nitrogen, and phosphorus are the most important of these nutrients, and C:N:P. ratios of 100:5:1 to 100:10:1 should be maintained in aerobic wastewater treatment and 250:5:1 in anaerobic wastewater treatment to ensure maximal microbial activity (Metcalf and Eddy, 2003). The C:N:P ratio in this study varied between 100:0.6:0.01 to 100:3.37:0.001 indicating a very poor C:N:P ratio that might render the ayurvedic pharmaceutical wastewater unfit for biological treatment.

The ayurvedic pharmaceutical wastewater can also be characterized generally by the presence of O and G. It is important to note here that the, during anaerobic treatment of wastewater, the O and G/COD ratio of more than 0.2 results in a reduction of system efficiency, biomass washout, and system failure (Miranda et al., 2005). In the present study, the O and G/COD ratio was found to be in the range of 0.3 to 8.5. Thus, while designing a wastewater treatment plant it is advisable to consider an industry on case to case basis. A few of the things which have to keep in mind are pH neutralization, O and G removal, and C:N:P ratio correction.

Biochemical Methane Potential (BMP)

For this study, fresh anaerobic sludge from the food waste bioreactor was used as an inoculum and its COD was 25,000 mg/L. As mentioned earlier, the inoculum-to-substrate ratio was maintained at 0.5. The results of the cumulative biogas generation from each of the industries are presented in Fig 3. As can be seen, the cumulative biogas generation was the highest (4031 mL after 20 days) for the wastewater from vessel washing of lehiyum. This is because of the high values of COD and BOD of lehiyum wastewater which were found to be 1,66,000 and 85,000 mg/L, respectively. This was followed by thailam wastewater (S7), mixed samples from industry 3 (S5), and raw effluent from industry 1 (P1). All the samples irrespective of their initial COD levels showed good biodegradability potential. This was also evident from the change in initial COD levels of the mixture of inoculum and substrate. The COD removal efficiency was found to be highest for P1 (64%) followed by S5 (54%), S6 (35%), and S7 (34%). It is imperative to mention here the reasons for biogas generation despite the poor C:N:P ratio and low pH. It is likely that the inoculum provided the cushioning for low pH and the necessary nutrients N and P were supplied from the inoculum to the anaerobic bacteria. The governing parameters such as pH, VFA, and alkalinity are presented in Fig 4.

Table 1. Physico-chemical characteristics of wastewater collected from ayurvedic pharmaceutical units.

Parameters	Industry 1	Industry 2					Industry 3	
	P1	S1	S2	S3	S4	S5	S6	S7
pH	5.9	2.9	6.8	5.1	4	5.1	4.4	10.3
TSS	279	1570	1902	3086	2610	1356	12910	19120
TDS	609	5780	7077	1473	10530	3145	100060	21780
COD	750	8225	2125	6652	12700	4571	166696	29038
BOD	466	4031	747.5	3400	4375	2250	85000	14400
TKN	4.76	56	62	5.6	28	22.4	140	980
TP	4.95	1.53	0.81	1.51	2.45	1.13	1.04	0.54
O and G	239	26634	3070	56569	22039	25278	33983	13643

Note: P1-Combined raw effluent, S1-Juice, S2-Pre-process, S3-Post-production, S4-Processongoing, S5-Mixed sample, S6-Lehiyum, S7-Thailum.

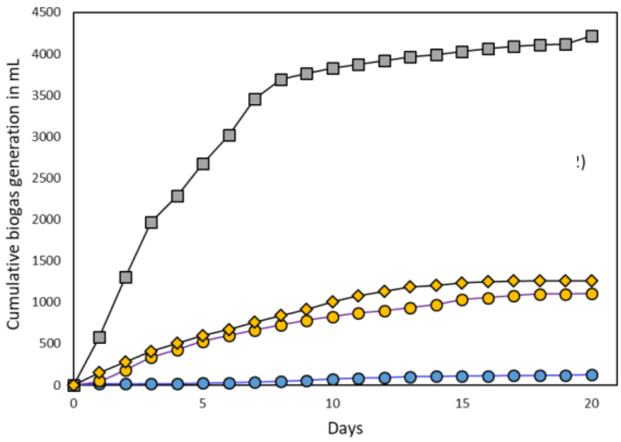

Fig. 3. Cumulative biogas generation from ayurvedic pharmaceutical wastewater. **Note:** (—●—) P1(Industry 1), (—●—) S5 (Mixed dample, Industry), (—■—) S6 (Lehiyum, Industry3), (—◆—) S7(Thailam, Industry 3).

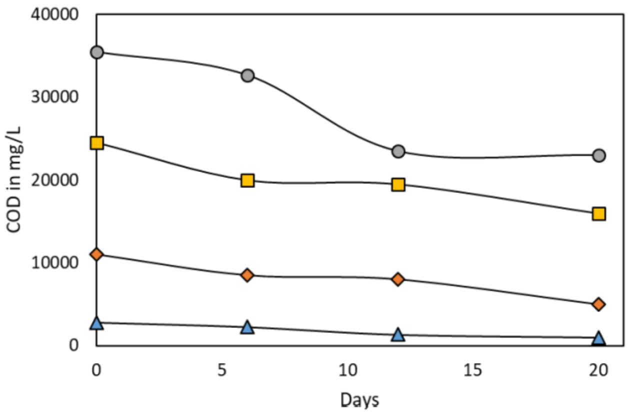

Fig. 4. Change in COD of the mixture of inoculum and substrate. **Note:** (—▲—) P1, (—◆—) S5, (—●—) S6, (—■—) S7

The pH during the entire test period was found to be near neutral for all the samples. The Volatile Fatty Acids (VFAs) are intermediate organic acids produced during anaerobic digestion. To prevent acidification during an anaerobic process, it is crucial to maintain a proper volatile fatty acids VFA/alkalinity ratio, which is why it should always be kept below 0.4. Whereas, the VFA/alkalinity ratio ≥ 1.0 yields carbon dioxide and hydrogen as the principal breakdown products (Hernández, et al., 2014). In this study, the VFA/alkalinity ratio was well below 0.4 indicating better process stability. It is important to mention here that the biogas generation could be improved if the test were conducted after removing O and G. As evident from Table 2. The O and G concentration in samples S5, S6 and S7 was between 13643 to 33983 mg/L which might have a negative effect on anaerobic bacteria resulting in less biogas yield.

Composition of Solid Residues and Oil Residue

The moisture contents of 68.88% and 69.43% were found in the solid residue from industries 1 and 3. In contrast, the solid and oil residue from industry 3 had a lower moisture content, of 6.51 percent. This is because the herbs were pressed using a squeezer as mentioned in section 2.4. As shown in Fig 5, the solid residue from industries 1 and 3 had 95.61 and 94.86% Volatile Solids (VS), and the solid+oil residue from industry 3 contains 85.4% VS on a dry weight basis. The Fixed Solids (FS) or the ash content was ranging between 4.39 to 14.6% on a dry weight basis. Table 3 represents the compositional analysis of lignocelluloses of solid residues and oil residue from industry 1 and industry 3. The general rule is that the age, storage duration, type of plant tissue, growing conditions, and harvesting conditions can all quantitatively affect the composition analysis of lignocellulosic materials within the same plant species (Szczerbowski, et al., 2014). From Table 3, it is clear that the major component in the solid residue was cellulose (34.45% to 41.69%) followed by lignin (31.46% to 38.72%). Since the moisture content of solid+oil residue is very low, it seems reasonable to say that the solid+oil residue can be directly used as a solid fuel since its VS content is also very high to the tune of 85.4% on a dry weight basis. Percentage of moisture content, dry solids, fixed solids, and volatile content of solid residues from Industry 1 and 3 and oil residue from Industry 3 Table 3. Compositional analysis of lignocelluloses of solid residues and oil residue Constituent Industry1 (solid residue was cellulose (34.45% to 41.69%) followed by lignin (31.46% to 38.72%). Since the moisture content of solid+oil residue is very low, it seems reasonable to say that the solid+oil residue can be directly used as a solid fuel since its VS content is also very high to the tune of 85.4% on a dry weight basis.

Table 2. Change in pH, VFA, and alkalinity during BMP test.

Samples	**P1**				**S5**			
Day	**pH**	**VFA**	**Alkalinity**	**VFA/Alkalinity**	**pH**	**VFA**	**Alkalinity**	**VFA/Alkalinity**
0	6.92	8.62	11.02	0.78	7.72	12.95	59.88	0.2
6	7.07	2	12	0.167	7.44	4.108	71.97	0.05
12	7.1	0.78	16.06	0.056	7.42	2.057	69.01	0.03
20	7.08	1.263	14.938	0.084	7.19	2.76	65.52	0.04
Samples	**S6**				**S7**			
0	7	54.2	156.7	0.34	7.59	15.88	201.65	0.07
6	7.65	15.2	207.7	0.07	7.65	10.98	226.88	0.05
12	7.62	1.22	197	0.006	7.54	51.08	196.03	0.26
20	7.68	7.97	196.457	0.04	7.65	6.19	185.54	0.03

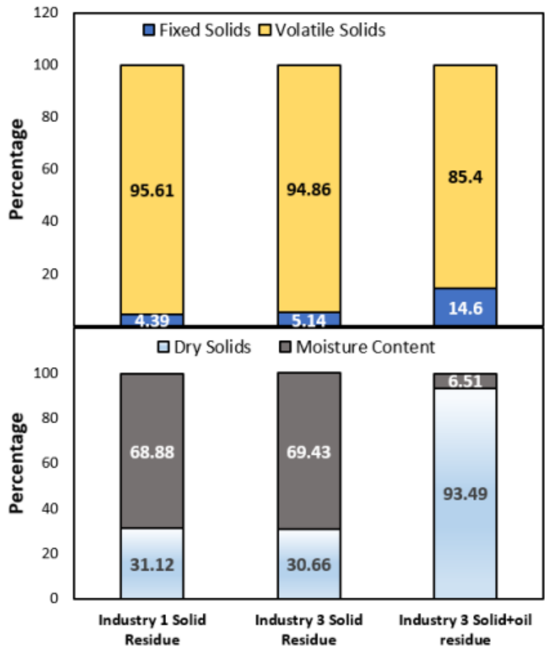

Fig. 5. Change in COD of the mixture of inoculum and substrate. **Note:** (-▲-) P1, (-◆-) S5, (-●-) S6, (-■-) S7

Table 3. Compositional analysis of lignocelluloses of solid residues and oil residue. (All values are expresses in percentage on a dry weight basis).

Constituent	**Industry 1 (solid residue)**	**Industry 3 (solid residue)**	**Industry 3 (oil residue)**
Cellulose	34.45	41.61	36.98
Hemicellulose	20.36	20.38	17.31
Total lignin	38.72	31.46	34.51
Ash content	1.1	1.47	1.05

As far as, the management of solid residue is concerned, the method of composting may not be a viable option. As stated by the bioconversion efficiency of lignocellulosic material is very poor because of its recalcitrant nature (Wu, et al., 2022). However, if the solid residues are dried either naturally or by mechanical means, the same can also be used a solid fuel since its VS content is nearly 95%.

CONCLUSION

The wastewater characteristics in terms of pH, O and G, organic load (COD and BOD) and nutrients (TKN and TP) differs greatly from industry to industry and it would be difficult to define or specify a definite range of concentrations for wastewater parameters. Nevertheless, it is noteworthy to mention that few traits of wastewater characteristics were common to all the industries and this includes low or acidic pH (2.9 to 6.8), high O and G concentration (~22,000 to 56,000 mg/l), and low levels of nutrients (TKN~5 to 60 mg/l and TP~0.8 to 5 mg/l). At the same time, the BOD/COD ratio was more or less oscillating between 0.3 and 0.6 for all the samples indicating moderate to good biodegradability of the wastewater. The results of the biochemical methane potential test were encouraging in terms of the ability of the wastewater to produce biogas. It was found that the cumulative biogas generation was 124 mL for initial COD of 750 mg/l; 1104 ml for initial COD of 4571 mg/l; 4214 mL for initial COD of 166696 mg/l and 1263 ml for initial COD of 29038 mg/l indicating the good potential to produce biogas. The various governing parameters of anaerobic treatment viz. pH, VFAs, alkalinity, and VFA/alkalinity ratio was found to be within the range indicating better process stability. Thus, anaerobic treatment of ayurvedic pharmaceutical wastewater can be regarded as an attractive option. It is reasonable to conclude that the wastewater treatment of ayurvedic pharmaceutical wastewater shall be considered on a case-to-case basis based only on the detailed physico-chemical characterization. The proximate analysis of the herbal residues from the Ayurvedic pharmaceutical industry showed that the moisture content was more than 65% for herbal residues and 6.51% for solid+oil residue. The volatile solids were around 95% for herbal residues and 85% for solid+oil residue on a dry weight basis. The biomass compositional analysis showed that the residue was mostly of lignocellulosic origin. The lignocellulosic biomass is hard to decompose and hence, it is better to dry the solid residue and used it as a fuel in solid fuel boilers

REFERENCES

Chauhan A, Semwal D, Mishra S and Semwal R. 2015. Ayurvedic research and methodology: Present status and future strategies. AYU. 36(4): 364-369.

Subrat N, Prasad R and Iyer M.2002. The ayurvedic medicine industry: Current status and sustainability. Ecotech Services.

Singh S, Singh S, Lo SL and Kumar N. 2016. Electrochemical treatment of Ayurveda pharmaceuticals wastewater: Optimization and characterization of sludge residue. J Taiwan Inst Chem Eng.67:385-396.

Ministry of AYUSH. 2018. Central Council for Research in Ayurvedic Sciences, Government of India, New Delhi.

Jain G, Satyanarayan S, Nawghare P, Kaul SN and Szpyrcowicz L. 2001. Treatment of pharmaceutical wastewater (herbal) by a coagulation/flocculation process. Int J Environ Sci. 58(3):313-330.

Silva Junior JOC, Ribeiro Costa RM, Martins F and Ramos Barbos WL. 2011. Processing and Quality Control of Herbal Drugs and Their Derivatives. Phytochem.11:196-222.

APHA. 2017.Standard methods for the examination of water and wastewater, 23rd ed. Washington, DC, USA: American Public Health Association.

Anderson GK and Yang G. 1992. Determination of Bicarbonate and Total Volatile Acid Concentration in Anaerobic Digesters Using a Simple Titration. Water Environ Res. 64(1): 53-59.

Papadopoulos A, Parissopoulos G, Papadopoulos F and Karteris A. 2001. Variations of COD/BOD5 Ratio at Different Units of A Wastewater Stabilization Pond Pilot Treatment Facility. 7th International Conference on Environmental Science and Technology Ermoupolis. 369-376.

Stoddard A, Harcum JB, Jonathan TS, James R, Pagenkopf R and Bastian K.2002. Municipal wastewater treatment- evaluating improvement in national water quality. John Wiley and Sons, New York.

Metcalf and Eddy Inc. 2003. Wastewater Engineering: Treatment and Reuse. Boston :McGraw-Hill.

Miranda LAS, Henriques JAP and Monteggia LO.2005. A full-scale UASB reactor for treatment of pig and cattle slaughterhouse wastewater with a high oil and grease content. Braz J Chem Eng. 22(4):601-610.

Hernández MA, Rodríguez Susa M and Andres Y. 2014. Use of coffee mucilage as a new substrate for hydrogen production in anaerobic co-digestion with swine manure. Bioresour Technol. 168: 112-118.

Szczerbowski D, Pitarelo AP, Zandoná Filho A and Ramos LP. 2014. Sugarcane biomass for biorefineries: Comparative composition of carbohydrate and non-carbohydrate components of bagasse and straw. Carbohydr Polym.114:95-101.

Wu D, Wei Z, Mohamed TA, Zheng G, Qu F, Wang F, Zhao Y and Song C. 2022. Lignocellulose biomass bioconversion during composting: Mechanism of action of lignocellulase, pretreatment methods and future perspectives. Chemosphere.286:131635.