

Study on Brazilian agribusiness wastewaters: composition, physical-chemical characterization, volumetric production and resource recovery

Estudo sobre águas residuárias do agronegócio brasileiro: composição, caracterização físico-química, produção volumétrica e recuperação de recursos

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ABSTRACT

Brazil is a significant producer of agricultural and agro-industrial waste, which can be used to recover valuable resources, such as struvite, hydroxyapatite, methane gas, hydrogen gas, and carboxylic acids, to mitigate the environmental impacts of the agro-industrial sector, add economic value to organic waste, and promote the sustainability of natural resources. Thus, this work's objective was to compile and analyze data on the composition, physical-chemical characterization, and volumetric production of six agricultural and agro-industrial wastewaters (AWWs) from activities of paramount importance in Brazilian agribusiness and to report studies on resource recovery from those liquid wastes. The literature review was carried out by analyzing scientific works obtained by searching for keywords in different databases. It was concluded that swine wastewaters (SWs), slaughterhouse wastewaters (SHWs), and dairy wastewaters (DWs) are the most promising for struvite recovery. DWs also stand out for the recovery of hydroxyapatite. SWs and brewery wastewaters (BWw) are commonly used for prospecting for algae or bacterial biomass and their derivative products. All AWWs analyzed are considered promising for biogas, methane and hydrogen, while the most soluble AWWs are more valuable for carboxylic acid production.

Keywords: nexus concept; organic liquid waste; environmental sustainability; agro-industrial wastewater; wastewater treatment.

RESUMO

O Brasil é um grande produtor de resíduos agrícolas e agroindustriais, os quais podem ser utilizados para a recuperação de recursos valiosos, como a estruvita, a hidroxiapatita, o gás metano, o gás hidrogênio e os ácidos carboxílicos, visando mitigar os impactos ambientais do setor agroindustrial, agregar valor econômico aos resíduos orgânicos e promover a sustentabilidade dos recursos naturais. Assim, o objetivo deste trabalho foi compilar e analisar dados de composição, de caracterização físico-química e de produção volumétrica de seis águas residuárias agrícolas e agroindustriais (ARA) provenientes de atividades de suma importância ao agronegócio brasileiro e reportar estudos sobre recuperação de recursos a partir desses resíduos líquidos. A revisão de literatura foi elaborada por meio da análise de trabalhos científicos obtidos mediante à busca de palavras-chave em diferentes bancos de dados. Concluiu-se que as águas residuárias da criação de suínos (ARCS), as águas residuárias de abate bovino (ARAB) e as águas residuárias do beneficiamento de leite (ARBL) são as mais promissoras para a recuperação de estruvita. As ARBL também se destacam para a recuperação de hidroxiapatita. As ARCS e as águas residuárias da produção de cerveja (ARPC) são comumente utilizadas para a prospecção de biomassa algácea ou bacteriana e seus produtos derivados. Todas as ARA analisadas são adequadas para a prospecção de biogás, metano e hidrogênio, enquanto as ARA mais solúveis são as mais promissoras para a produção de ácidos carboxílicos.

Palavras-chave: conceito *nexus*; resíduos líquidos orgânicos; sustentabilidade ambiental; águas residuárias agroindustriais; tratamento de águas residuárias.

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Introduction

According to the Center for Advanced Studies in Applied Economics at the University of São Paulo (Centro de Estudos Avançados em Economia Aplicada da Universidade de São Paulo — CEPEA/USP) and the National Confederation of Agriculture and Livestock of Brazil (Confederação Nacional da Agricultura e Pecuária do Brasil — CNA), in the first half of 2020, Brazil was the fourth largest exporter of agricultural products in the world, second only to the European Union, the United States of America (USA) and China. It was also a world leader in coffee production and a leader in the export of sugar, coffee, orange juice, soybeans, beef and chicken, showing agribusiness as one of the main activities that sustain the Brazilian economy (CNA, 2020).

In 2019, agribusiness was responsible for 43% of national exports, 21.4% of the Brazilian gross domestic product (GDP), and generating more than 18.2 million jobs, corresponding to 19.54% of the employed population with and without formalization (CEPEA and CNA, 2020). The share of agribusiness in the national GDP increased from 20.8% to 21.4% between 2018 and 2019 and showed a growth of 1.9% of GDP in the first quarter of 2020 compared to the same period of 2019 (Barros et al., 2020).

Due to agro-industry growth, there is an increasing generation of liquid organic waste, such as agricultural and agro-industrial wastewaters (AWWs), in production processes and related activities. These residues cause environmental impacts when they are not treated and disposed of properly, which contributes to soil, air and water pollution, contributing to the eutrophication of water bodies, in addition to causing possible harm to human and animal health (Dornelles et al., 2017; Morais et al., 2020b). Only dairy wastewaters generated worldwide, for example, have a polluting potential equivalent to 60% of the world population (Silva et al., 2020a).

In addition to the high generation of effluents from agribusiness activities, it is estimated that the global demand for water, energy and food will increase by more than 50% by 2050 compared to 2015 (Zhang et al., 2018). Such demand, driven by rapid population growth, urbanization, climate change and the depletion of fossil fuels, requires the adoption of solutions or alternatives that allow global resources management in a comprehensive, interconnected and efficient manner. Thus, the nexus water-energy-food concept was designed to study how these three systems are related and propose integrated planning strategies to optimize the use of natural resources in a sustainable way (Zhang et al., 2018).

In this context, aiming not only to mitigate the environmental impacts caused by its inadequate disposal but also to add economic value to organic liquid waste, the development of new treatment technologies and the study of the characteristics and potential of production and resource recovery from AWWs and other wastes have become essential to the progress of society and the maintenance of environmental resources (Bustillo-Lecompte and Mehrvar, 2015).

Thus, wastewater treatment can be directed towards the production and recovery of resources of commercial and industrial interest, such as struvite, hydroxyapatite, methane (CH_4), hydrogen (H_2), and carboxylic acids (Song et al., 2018). In this scenario, due to the high agricultural and agro-industrial activity in Brazil, it is essential to analyze the potential for prospecting these resources from different residues, stimulating the design and implementation of treatment plants with resource recovery.

Accordingly, scientific studies on resource recovery from AWWs can be facilitated by reviewing the technical literature that provides scientists with fundamental knowledge for developing their research. Despite several scientific studies on the treatment of AWWs, data on the composition and physical-chemical properties are dispersed in the literature and, generally, are reported superficially in applied research.

Thus, this work's objective was to compile and analyze data on the composition, physical-chemical characterization, and volumetric production of six agricultural and agro-industrial wastewaters from activities of paramount importance in Brazilian agribusiness and to report studies on resource recovery from those liquid wastes.

Methodology

Agricultural and agro-industrial wastewaters

The AWWs analyzed in this work were: slaughterhouse wastewaters (SHWs), swine wastewaters (SWs), brewery wastewaters (BW), dairy wastewaters (DWs), fruit processing wastewaters (FPWs) from the production of ice cream and biodiesel production wastewaters (residual glycerol – RG).

It is already consolidated in the technical literature that these AWWs can be used to recover bioenergy from anaerobic methane production (Silva et al., 2020a), demonstrating the potential of these liquid residues for the recovery of other bioproducts. Thus, the possibility of recovering resources from low-cost substrates prompted us to investigate these AWWs and to build a literature review compiling data on their composition, physical-chemical characterization and volumetric production, aiming to provide researchers, in an only material, fundamental knowledge about each wastewater evaluated and to stimulate the development of new scientific research.

Resource recovery studies

The technical literature reports several chemical, physical and biological processes in which AWWs can be submitted aimed at the production and prospecting of resources. Due to the impossibility of deepening and discussing all the strategies reported in the literature, the most common ones were adopted in the context of wastewater treatment, such as anaerobic and aerobic biological treatment. In addition to these, in the context of nutrient removal, the chemical precipitation process was selected (Chernicharo, 2007; Metcalf and Eddy, 2016).

On the basis of scientific studies reporting the use of AWWs for resource recovery, a significant amount of research has been observed associated with the removal of nutrients from the recovery of minerals (such as struvite and hydroxyapatite), the production of biomass for the prospecting of compounds of industrial interest (such as algal biomass) and the production and extraction of compounds commonly exploited in the anaerobic digestion of organic waste (methane, hydrogen and carboxylic acids, for example). Therefore, these resources were chosen for detail in this review. Thus, on the basis of the composition and physical-chemical characterization of the AWWs selected for evaluation, one can analyze which ones are most promising for obtaining these resources.

Data collection

The literature review was carried out through the analysis of scientific articles and other academic works, such as monographs, master's dissertations, and doctoral theses, obtained by searching keywords in different databases, such as SciVerse Scopus, Google Scholar, SciELO, Science Direct and CAPES Journals (Higher Education Personnel Improvement Coordination Journals – Periódicos da Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – CAPES). The data survey took place between January and July 2020.

The main keywords used (in English and in Portuguese) in the databases to search for scientific works were: slaughterhouse wastewaters (*águas residuárias de abate bovino*), swine wastewaters (*águas residuárias da criação de suínos*), brewery wastewaters (*águas residuárias da produção de cerveja*), dairy wastewaters (*águas residuárias do beneficiamento de leite*), fruit processing wastewaters (*águas residuárias do beneficiamento de frutas*), residual glycerol (*glicerol residual*), methane (*metano*), hydrogen (*hidrogênio*), carboxylic acids or volatile fatty acids (*ácidos carboxílicos*), algae biomass (*biomassa algácea*), struvite (*estruvita*) and hydroxyapatite (*hidroxiapatita*). Context-related words were also used, such as slaughterhouse (*abatedouro*), swine farming (*suinocultura*), brewery (*cervejaria*), dairy (*laticínios*), fruit processing (*beneficiamento de frutas*), ice cream (*sorvetes*), and glycerol (*glicerol*). These words were combined in different ways to carry out the research.

For the selection of scientific articles, the summary and objectives of each one were read. Subsequently, articles that contained data on the composition, physical-chemical characterization, volumetric production of raw wastewaters and those that addressed resource recovery using these AWWs were selected. The publication date was another selection criterion used, considering only articles published between 1990 and 2020. However, preference was given to collecting data reported in papers published since 2010 in international journals with scientific relevance. Articles with cross-cutting themes were also selected, such as environmental pollution, the nexus concept, biological treatment of wastewater and bioproducts, to support the introduction and discussion. The choice of articles published in recent years (2015 to 2020) was prioritized.

Through consultation with electronic portals (websites), technical and economic reports were also obtained and analyzed from different relevant institutes or organizations, such as the Brazilian Institute of Geography and Statistics (Instituto Brasileiro de Geografia e Estatística — IBGE), the Food and Agriculture Organization of the United Nations (FAO), the Ministry of Agriculture, Livestock and Supply (Ministério da Agricultura, Pecuária e Abastecimento — MAPA), the Center for Advanced Studies in Applied Economics (Centro de Estudos Avançados em Economia Aplicada — CEPEA) and the National Confederation of Agriculture and Livestock (Confederação Nacional da Agricultura e Pecuária — CNA). In this case, only works published since 2016 were considered to provide more recent information on the evaluated agribusiness activities' economic aspects.

The Statista portal (<https://www.statista.com/>), which consists of a statistics and infographics platform for consultation, was also used in data collection in some cases. After selecting scientific papers, the data of interest were compiled, and the review article was constructed.

Composition, Physical-Chemical Characterization and Volumetric Production of Agricultural and Agro-Industrial Wastewaters

Table 1 summarizes the importance of some Brazilian agribusiness activities in a national and international panorama based on 2017 and adjacent years. This table also presents a range of volumetric production for each AWW. Figure 1 shows the leading Brazilian states that produce these wastes. It is noticed that these agribusiness sectors are concentrated in the South, Southeast and Midwest regions.

The constant generation of wastewaters from cattle slaughter (slaughterhouse wastewater — SHWs) and swine farming (swine wastewaters — SWs) is the result of the growing demand for livestock products due to the high nutritional value of meat (proteins, minerals, and bioavailable vitamins), which is a crucial part of the diet of the population of several countries, including Brazil (Moukakis et al., 2018).

SHWs are generally composed of blood, manure and viscera and contain a high proportion of proteins and lipids, thus having a high amount of biodegradable organic matter (Fia et al., 2015). Furthermore, SHWs have a high concentration of pathogenic and non-pathogenic microorganisms and can promote ecotoxicity at acute and chronic levels, which makes the treatment of this effluent indispensable before it is disposed of in water bodies (Pereira et al., 2016). SHWs may also contain heavy metals and residues of cleaning agents and veterinary medical products, which is why they are considered highly polluting worldwide due to their complex composition and high volumetric production (Souza and Orrico, 2016).

In the same sense, SWs are complex liquid wastes that can be defined as a mixture of wasted feed, water spilled from drinking fountains, animal excrement (feces and urine) and water used for cleaning and hygiene purposes in swine farming.

Table 1 – National and international relevance and range of volumetric production of wastewaters generated by Brazilian agribusiness activities, based on 2017 and adjacent years.

Agribusiness activities	National relevance	International relevance	Volumetric production	References
Cattle slaughter	It is estimated that in 2017, 30.8 million heads were slaughtered. The actual bovine data in 2018 indicate that the country had, in that year, 222.0 million head. In 2019, Brazil was the largest beef exporter, with around 2.00 million tons, and the second largest producer, with 9.90 million tons.	In 2017, world beef production totaled 70 million tons. Meat production is dominated by Brazil, China, the European Union, the Russian Federation and the United States.	During the bovine slaughter process, about 3 m ³ of wastewater are generated, on average, by slaughtered cattle. A processing facility can consume between 2.5 and 40 m ³ of water per ton of meat produced.	Bustillo-Lecompte and Mehrvar (2015) Pereira et al. (2016) Brasil (2018) CNA (2020)
Swine farming	Around 3.75 million tons of pork were produced in 2017, making Brazil fourth in world production. In 2019, Brazil was the fourth largest pork producer and exporter, making 3.70 million tons available on the national market and exporting 0.7 million tons.	World net pork production totaled around 109.85 million tons of carcass weight in 2016, with production dominated by China, the European Union, the United States and Brazil.	It is estimated that 4 - 9 L of wastewater are generated daily by swine on a farm.	García et al. (2017) USDA (2018) Nagarajan et al. (2019) CNA (2020)
Beer production	Brazil produces about 13 billion L of beer per year. In 2016, 140 million hL of beer were produced in the country, giving Brazil third place worldwide.	In 2017, global beer production reached around 1.95 billion hL, compared to 1.3 billion hL in 1998. The main countries in beer production are China, the United States and Brazil.	It is estimated that for each liter of beer produced, 4.5 - 10 L of wastewater are generated.	Marcusso and Müller (2017) Arantes et al. (2017) Pachiega et al. (2019) Statista (2019a)
Milk processing and production of derivatives	In 2017, Brazil produced around 35.1 billion liters of milk. Over four decades, national production has quadrupled. Sales of dairy products abroad were mostly powdered milk (62.2%), UHT milk (18.7%) and different types of cheese (9.1%).	World milk production reached 811 million tons in 2017. The world's top five milk producers are the European Union (20%), India (20%), the United States (12%), Pakistan (6%) and China (5%).	The dairy and milk processing industry produces 0.2 - 10 L of wastewater per liter of milk processed.	Fernandes and Naval (2017) EMBRAPA (2018) FAO (2018) OECD and FAO (2018) Silva, A.N. et al. (2019)
Fruit processing for ice cream production	In 2017, about 1,129 million L of ice cream were produced, with a per capita consumption of 5.44 L per year, making Brazil the sixth leading country worldwide in consumption (3.1%).	In 2017, the global ice cream market had an estimated value of 56.91 million USD. By 2024, it is expected to be worth 74.96 billion USD.	The ice cream industry generates 3 - 7 L of wastewater per 0.45 kg of ice cream produced.	Enteshari and Martínez-Monteagudo (2018) ABIS (2019) Statista (2019b)
Biodiesel production	In 2017, biodiesel production was 4.3 million m ³ , which corresponded to 56.2% of the total national production capacity (21.2 thousand m ³ per day). That same year, 374,500 m ³ of glycerol were generated as a by-product of biodiesel production.	The global production of biodiesel was just over 34 million tons in 2016. The most important producer of biodiesel is the European Union, followed by the United States and Brazil.	For every 90 m ³ of biodiesel produced by transesterification, 10 m ³ of glycerol are generated.	Mota et al. (2009) Yazdani and Gonzalez (2007) ANP (2018) UFOP (2017)

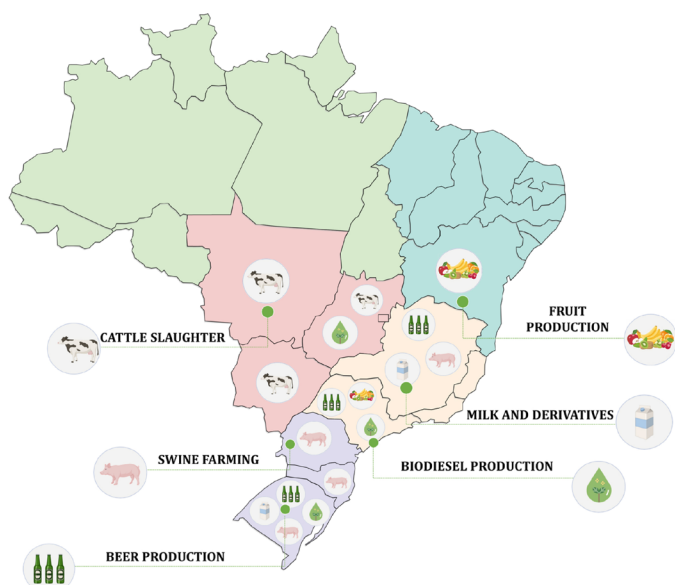


Figure 1 – Leading Brazilian states producing agricultural and agro-industrial wastewaters.

Source: adapted from Marcusso and Müller (2017), EMBRAPA (2018), ANP (2018), ABIS (2019) and CNA (2020).

For this reason, SWs are characterized by having high levels of organic matter, suspended solids, nutrients and high microbial load (Pereira et al., 2009). SWs can also contain considerable concentrations of antibiotics (tetracyclines, sulfonamides and macrolides) and hormones (estrogens, androgens, glucocorticoids and progestogens), extensively used to treat infections and even used as promoters of animal growth. For this reason, this type of AWW can introduce micropollutants, such as antibiotics and hormones, indiscriminately into the environment (Cheng et al., 2018).

In another perspective, the beverage sector makes up a fundamental part of the agribusiness in the national and international panorama, emphasizing the production of soft drinks, coffee, beer and milk (Cervieri Júnior et al., 2014). In this type of industry, a large amount of water is used to produce beverages, washing bottles and cleaning equipment and machines, with an estimated 50% of the total wastewater generated coming from washing bottles. Thus, the beverage sector contributes to the generation of polluting liquid effluents due to the high concentrations of sugars and other biodegradable compounds derived from its production process (Abdel-Fatah et al., 2017).

In the beverage sector, beer is the fifth most consumed beverage globally, behind tea, soda, milk and coffee (Olajire, 2012). The beer industry generates residues called wastewaters from beer production (brewery wastewaters – BWs), containing residual amounts of raw materials for the drink, including suspended solids, sugars and yeasts. BWs come from the beer production chain's unitary operations, such

as filtration, equipment discharges, container washing and cleaning of tanks, vats, pipes, and floors (Arantes et al., 2017).

On the other hand, the dairy industry is one of the largest sectors of food processing and, for this reason, consumes large amounts of water for cleaning and sanitizing machines and equipment, exchanging heat and washing its locations. Wastewaters from milk processing (dairy wastewaters – DWs) and derived products are composed of wasted milk residues, lactose, fats, nutrients and residues of detergents and disinfectants. Depending on the season and the production system, the characterization of DWs varies considerably (Chandra et al., 2018; Daneshvar et al., 2019).

Still in the context of the food industry, ice cream is one of the most popular luxury items in the world and the sector is overgrowing (Konstantas et al., 2019). During the washing and pulping of fruits for ice cream production, liquid residues referred to as wastewaters from the processing of fruits for ice cream production (fruit processing wastewaters – FPWs) are generated. These consist of a complex colloidal mixture of suspended solids (flavoring compounds), soluble molecules (carbohydrates, milk proteins and other sources, lipids and minerals) and detergent and disinfectant residues (Demirel et al., 2013).

Biodiesel is increasingly considered an environmentally viable substitute for diesel in the biofuels business due to global energy needs. Residual glycerol from biodiesel plants (RG) is a by-product of the manufacture of this biofuel from a transesterification reaction of oils (vegetables or animals) with alcohol (Pereira et al., 2019). Besides having a high organic load, the generated RG includes many impurities and chemicals, such as methanol, organic and inorganic salts, vegetable dyes, traces of mono- and diglycerides and soap, making it a polluting by-product (Anitha et al., 2016).

Due to the importance of the agro-industrial activities shown in Table 1 and the environmental impacts potentially caused by them, it is essential to know the physical-chemical characteristics of raw AWWs generated in their production processes. Table 2 summarizes the main physical-chemical characteristics of raw AWWs reported in the technical literature.

According to data expressed in Table 2, there is significant variability in the physical and chemical characteristics of AWWs due to the production processes, the routine inherent to each agribusiness and the sustainability practices adopted (Ranade and Bhandari, 2014). Despite this variability, all of them have high levels of organic matter and nutrients, not meeting the effluent release standards established by the federal legislation in force in Brazil (Brasil, 2011), showing that they must be treated before being disposed of in the environment (Morais and Santos, 2019).

Resource Recovery from Agricultural and Agro-Industrial Wastewaters

The following topics will briefly present an overview of resource recovery from the AWWs evaluated in this work, mainly discussing these resources' industrial applications.

Table 2 – Range of values of physical-chemical characteristics of raw agricultural and agro-industrial wastewaters evaluated.

AWWs	Parameter	Value range	Unit	References
SHWs	pH	4.9–8.1	-	Bustillo-Lecompte and Mehrvar (2015) Pereira et al. (2016) Plácido and Zhang (2018) Morais (2019) Morais et al. (2020b) Morais et al. (2021)
	Al	83–1,500	mg L ⁻¹ CaCO ₃	
	COD	1,018–13,800	mg L ⁻¹ O ₂	
	BOD	420–5,770	mg L ⁻¹ O ₂	
	TN	50–840	mg L ⁻¹	
	N-NH ₄ ⁺	20–340	mg L ⁻¹	
	TP	20–2,260	mg L ⁻¹	
SWs	pH	7.0–8.5	-	Suto et al. (2017) Ding et al. (2017) Cheng et al. (2018) Xiao et al. (2018) Morais et al. (2020a)
	Al	560–4,780	mg L ⁻¹ CaCO ₃	
	COD	3,000–30,000	mg L ⁻¹ O ₂	
	BOD	1,500–8,700	mg L ⁻¹ O ₂	
	TN	800–6,000	mg L ⁻¹	
	N-NH ₄ ⁺	400–2,000	mg L ⁻¹	
	TP	100–1,400	mg L ⁻¹	
BW _s	pH	5.0–11.0	-	Shi et al. (2010) Bakare et al. (2017) Arantes et al. (2017) Enitan et al. (2018) Silva, A.S. et al. (2019)
	Al	190–3,170	mg L ⁻¹ CaCO ₃	
	COD	2,000–32,500	mg L ⁻¹ O ₂	
	BOD	1,200–3,600	mg L ⁻¹ O ₂	
	TN	25–450	mg L ⁻¹	
	N-NH ₄ ⁺	5–22	mg L ⁻¹	
	TP	0.5–20	mg L ⁻¹	
DW _s	pH	4.7–1.0	-	Lu et al. (2016) Justina et al. (2018) Murcia et al. (2018) Daneshvar et al. (2019) Coelho et al. (2020b)
	Al	140–620	mg L ⁻¹ CaCO ₃	
	COD	80–95,000	mg L ⁻¹ O ₂	
	BOD	40–48,000	mg L ⁻¹ O ₂	
	TN	14–380	mg L ⁻¹	
	N-NH ₄ ⁺	1–48	mg L ⁻¹	
	TP	9–280	mg L ⁻¹	
FPWs	pH	3.2–7.7	-	Borja and Banks (1994) Borja e Banks (1995) Hu et al. (2002) Demirel et al. (2013) Morais et al. (2020b)
	Al	220–1,500	mg L ⁻¹ CaCO ₃	
	COD	4,500–10,480	mg L ⁻¹ O ₂	
	BOD	1,620–2,450	mg L ⁻¹ O ₂	
	TN	145–165	mg L ⁻¹	
	N-NH ₄ ⁺	32–43	mg L ⁻¹	
RG	pH	3.7–10.3	-	Sittijunda and Reungsang (2012) Oliveira et al. (2015) Silva et al. (2017) Ren et al. (2017) Pan et al. (2019) Coelho et al. (2020a)
	COD	1,023–1,260	g L ⁻¹ O ₂	
	TN	0–500	mg L ⁻¹	
	N-NH ₄ ⁺	5–50	mg L ⁻¹	
	TP	53–90	mg L ⁻¹	

pH: hydrogenionic potential; Al: total alkalinity; COD: chemical oxygen demand; BOD: biological oxygen demand; TN: total nitrogen; N-NH₄⁺: ammonium nitrogen; TP: total phosphorus.

The constructive and operational aspects of treatment technologies and resource prospecting will not be analyzed. Table 3 presents a compilation of recent studies that aim to treat AWWs with production and resource recovery.

Production of struvite and hydroxyapatite by chemical precipitation

AWWs have considerable concentrations of nutrients, such as phosphorus (P) and nitrogen (N). These nutrients can be recovered in the forms of orthophosphates (PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , H_3PO_4) and ammonium nitrogen (N-NH_4^+), respectively, through solid precipitates, such as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$). The great interest in the biorefinery of these nutrients is since they can be applied in the production of fertilizers for the agricultural industry and as building block chemicals in the chemical in-

dustrial for the production of nylon, plastic, explosives, rocket fuels and animal feed supplements (Carey et al., 2016).

Struvite is considered a slow-release fertilizer, being less soluble in water, and it contains low levels of heavy metals compared to conventional fertilizers, causing less severe environmental impacts on groundwater and water bodies (Wang et al. 2005). The recovery of struvite from AWWs provides the advantage of simultaneously removing phosphorus and nitrogen, depending on the composition of the AWWs, and has been extensively studied for a variety of liquid effluents, especially wastewaters from animal husbandry, particularly swine farming (in the case of struvite), and for effluents from the dairy and soft drink industry as well (Muhmood et al., 2019).

Recently, Kwon et al. (2018) investigated nitrogen and phosphorus removal via struvite formation by treating SWs (initial concentrations of ammonia and phosphate of 3.141 and 60.8 mg L⁻¹,

Table 3 – Research on resource recovery from agricultural and agro-industrial wastewaters evaluated in this study.

AWWs	Technology	Recovered resource	Efficiency of resource recovery process	References
SHWs	Anaerobic membrane bioreactor (AnMBR)	CH ₄	95% COD removal. Yield of CH ₄ : 365 L per kg COD applied.	Jensen et al. (2015)
	Tubular anaerobic digestors	Biogas	COD removal: more than 70%. Maximum biogas production: 0.2 m ³ m ⁻³ d ⁻¹ .	Martí-Herrero et al. (2018)
	Pilot scale two-stage anaerobic digesters	CH ₄	68.5% COD removal. Maximum CH ₄ yield: 384 mL per g COD applied.	Wang et al. (2018)
	Microbial fuel cell with aerobic and anaerobic bioreactors	Bioelectricity and nitrogen	99% COD removal efficiency. Generation of 162.55 mW m ⁻² of bioelectricity and 100% nitrogen recovery.	Mohammed and Ismail (2018)
	Batch anaerobic reactor Fed-batch anaerobic reactors Semi-continuous anaerobic reactors	CAs	Maximum concentration obtained of 100 g L ⁻¹ CAs. The predominant acids were C2, C4 and iso-C5.	Plácido and Zhang (2018)
	Batch anaerobic reactor	CAs	On average, 76% of the applied COD was converted to CAs. Yield 0.76 mg COD per mg COD applied.	Morais (2019)
SWs	Microbial electrolysis cell (MEC)	H ₂	69-75% COD removal. Productivity: 0.9 - 1.0 m ³ m ⁻³ d ⁻¹ H ₂ .	Wagner et al. (2009)
	Photobioreactor	Biomass and carbohydrates	60-70% COD removal. 40-90% removal of NH ₄ ⁺ -N. 3.96 g L ⁻¹ of maximum biomass concentration and 58% dry weight in carbohydrates.	Wang et al. (2015)
	Anaerobic sequential batch reactor (ASBR)	CH ₄	Maximum CH ₄ production rate: 1.952 L L ⁻¹ d ⁻¹ .	Yang et al. (2016)
	Constructed wetlands (CWs)	Nitrogen	87.7–97.9% removal for N-NH ₄ ⁺ and 85.4–96.1% for TN. Nitrogen recovery: of 120–222 g m ⁻² year ⁻¹ .	Luo et al. (2018)
	Anaerobic digester	Struvite	Removal of ammonia and phosphorus of 91.95 and 99.65%, respectively, with struvite formation in the molar ratio of 1.2 (Mg ²⁺): 1.0 (P-PO ₄ ³⁻): 1.0 (N-NH ₃).	Kwon et al. (2018)
	Batch anaerobic reactor	CAs	On average, 40% of the applied COD was converted to CAs. Yield 0.40 mg COD per mg COD applied.	Morais et al. (2020a)

Continue...

Table 3 – Continuation.

AWWs	Technology	Recovered resource	Efficiency of resource recovery process	References
BW _s	Batch anaerobic reactor	H ₂	Maximum H ₂ yield: 149.6 mL per g COD applied.	Shi et al. (2010)
	Upflow anaerobic sludge blanket (UASB) reactor	CH ₄	The highest rate of CH ₄ production occurred at 29 °C. Methane production rate increased from 0.29 to 1.46 L g COD ⁻¹ , when the loading rate was increased from 2.0 to 8.26 g COD L ⁻¹ d ⁻¹ .	Enitan et al. (2015)
	Immobilized-cells continuously stirred tank reactors (immobilized-cells CSTR)	H ₂ and energy	The maximum rate of H ₂ production of 55 L L ⁻¹ d ⁻¹ was obtained in hydraulic detention time of 1.5 h. High energy efficiency with an energy production rate of 641 kJ L ⁻¹ d ⁻¹ .	Sivagurunathan et al. (2015)
	Anaerobic membrane bioreactor (AnMBR)	CH ₄	Removal efficiency of 98% COD with 0.53 L of biogas per g COD removed. Biogas composition: 59% CH ₄ , 31% CO ₂ and 10% N ₂ .	Chen et al. (2016)
	Upflow anaerobic sludge blanket (UASB) reactor	CH ₄	78.97% COD removal; 60.21% BOD removal; CH ₄ corresponded to about 60-69% of the biogas.	Enitan et al. (2018)
	Photosynthetic bacterial-membrane bioreactor (PS-MBR)	Algal biomass, bacterial biomass and derived products	COD removal above 97%. Yields of biomass, proteins, polysaccharides, bacteriochlorophyll and coenzyme Q10 were respectively 0.51, 0.21, 0.089, 0.0013, 0.0054 and 0.019 g per g COD removed.	Lu et al. (2019)
	Batch anaerobic reactor	CAs	On average, 76% of the applied COD was converted. Yield of 0.60 g acids per g COD applied.	Silva, A.S. et al. (2019)
DW _s	Fed-batch anaerobic Reactors	Struvite	Recovery of 89% ammonia and 93% phosphate in various compounds, such as struvite.	Krishan and Srivastava (2015)
	Photobioreactor	Biodiesel and CAs	Maximum COD, TN, and TP removal rates obtained in indoor conditions were 88.38, 38.34, and 2.03 mg L ⁻¹ d ⁻¹ .	Lu et al. (2015)
	Two-stage anaerobic reactors	H ₂ and CH ₄	64% COD removal. Yield of H ₂ : 105 mL per g COD applied. Yield of CH ₄ : 190 mL per g COD applied.	Kothari et al. (2017)
	Combined system: continuously stirred tank reactor (CSTR) and compartmented anaerobic reactor	Biogas	82% COD removal. Yield of Biogas: 0.26 m ³ per kg COD removed.	Jürgensen et al. (2018)
	Anaerobic fluidized-bed reactor (AFBR)	H ₂	32.2% COD removal. Maximum H ₂ productivity: 0.80 L h ⁻¹ L ⁻¹ .	Silva, A.N. et al. (2019)
	Batch anaerobic reactor	CAs	On average, 83% of the COD applied was converted to CAs. Yield of 0.83 mg COD per mg COD applied.	Coelho et al. (2020b)
FPW _s	Upflow anaerobic sludge blanket (UASB) reactor	CH ₄	87% TOC removed. Yield of CH ₄ : 0.93 m ³ per kg TOC removed.	Goodwin et al. (1990)
	Upflow anaerobic sludge blanket (UASB) reactor	Biogas	Biogas yield: 0.31 - 0.52 L g ⁻¹ COD. 48.2% - 71.0% of CH ₄ in biogas.	Borja and Banks (1994)
	Anaerobic filter	CH ₄	70% COD removal. Yield of CH ₄ : 0.36 m ³ per kg COD removed.	Hawkes et al. (1995)
	Batch anaerobic reactor	CH ₄	Yield of CH ₄ : 0.338 L per g COD removed. Percentage of methane in biogas: 70%.	Demirel et al. (2013)
	Batch anaerobic reactor	CH ₄	Yield of CH ₄ : 0.283 L per g COD removed and 0.228 L per g COD applied. Biogas rich in CH ₄ (83.7%).	Morais (2019)

Continue...

Table 3 – Continuation.

AWWs	Technology	Recovered resource	Efficiency of resource recovery process	References
RG	Upflow anaerobic sludge blanket (UASB) reactor	H ₂	Total energy conversion efficiency of 44.8%. Maximum H ₂ productivity: 6.2 mmol L ⁻¹ h ⁻¹ .	Sittijunda and Reungsang (2012)
	Batch anaerobic reactor	CAs	Yield 0.51 g COD per g COD applied. Maximum CAs concentration: 38.5 g COD L ⁻¹ .	Yin et al. (2016)
	Photobioreactor	Biomass and lipids	Average biomass production of 16.7 g m ⁻² d ⁻¹ , lipid content of 23.6%, and the removal of 2.4 g m ⁻² d ⁻¹ N-NH ₄ ⁺ , 2.7 g m ⁻² d ⁻¹ TN, 3.0 g m ⁻² d ⁻¹ TP, and 103.0 g m ⁻² d ⁻¹ of COD.	Ren et al. (2017)
	Upflow anaerobic sludge blanket (UASB) reactor	H ₂	Total energy conversion efficiency of 63.63%. Yields of 368 mmol H ₂ per mol glycerol, 55 mmol H ₂ per L of 1,3-PDO, and 71 mmol H ₂ per L of ethanol.	Sittijunda and Reungsang (2017)
	Batch anaerobic reactor	CAs and 1,3-PDO	Production of C2, C3, C4, C5, C6 and 1,3-PDO at concentrations of 0.21, 0.50, 0.50, 2.31, 3.84 and 1.62 g L ⁻¹ , respectively. Conversion of 100% glycerol.	Dams et al. (2018)
	Batch anaerobic reactor	CAs	On average, 82% of the COD applied was converted to CAs. Yield 0.82 mg COD per mg COD applied.	Coelho (2019)

COD: chemical oxygen demand; BOD: biological oxygen demand; CAs: carboxylic acids; TOC: total organic carbon; TN: total nitrogen; N-NH₄⁺: ammonium nitrogen; TP: total phosphorous; CH₄: methane; H₂: hydrogen; C2: acetic acid; C3: propionic acid; C4: butyric acid; iso-C5: isovaleric acid; C5: valeric acid; C6: caproic acid; 1,3-PDO: 1,3-propanediol.

respectively) in an anaerobic digester. The authors obtained ammonia and phosphorus removal efficiency of 91.95 and 99.65%, respectively, with the formation of struvite in the molar ratio of 1.2 (Mg²⁺):1.0 (P-PO₄³⁻):1.0 (N-NH₃). Krishan and Srivastava (2015) established the same objective as the aforementioned authors, but treating DWs (initial concentrations of ammonia and phosphate of 69.96 and 45.05 mg L⁻¹, respectively) in an anaerobic batch reactor and achieved recovery of 89% ammonia and 93% phosphate in the form of various compounds together with struvite.

For the efficient recovery of struvite from AWWs that have low concentrations of magnesium and phosphorus about ammonium nitrogen concentrations, it is necessary to supplement magnesium and phosphorus salts, since, theoretically, the molar ratio 1:1:1 of Mg:N:P is a requirement for its precipitation (Muhmood et al., 2019).

Among the AWWs presented in this work, the SWs would be the most promising for the recovery of struvite due to the high levels of total nitrogen (800–6,000 mg L⁻¹ N) and total phosphorus (100–1,400 mg L⁻¹ P) commonly found in its composition (Kumar and Pal, 2015; Ding et al., 2017), which confirms the struvite recovery potential widely reported in the literature for this type of AWW (Suzuki et al., 2007; Wang et al., 2019). However, it is expected that it will be necessary to supplement the reaction medium with magnesium, since studies show that, in general, SWs are rich in ammonium and phosphate, while their magnesium content is low (Muhmood et al., 2019).

Despite this, the recovery of phosphorus as struvite is not always possible or appropriate since the precipitation of this compound competes with the precipitation of hydroxyapatite when the Ca²⁺/P molar ratio is greater than 1, which can be a problem in the recovery of struvite in AWWs that include calcium in their composition (Monballiu et al., 2018). Ca²⁺ ions block struvite's growth surface, thus impairing its formation (Pastor et al., 2008). Tao et al. (2016) reported that a high Ca²⁺/Mg²⁺ molar ratio (greater than 0.5) causes a competitive environment between the formation of struvite and calcium-based phosphate products, causing adverse impacts on the formation of struvite.

Accordingly, Hakimi et al. (2020) evaluated the recovery of struvite from SHWs using an anaerobic membrane bioreactor (AnMBR). They reported that the molar ratio Mg²⁺/Ca²⁺ of 0.8 (high concentration of calcium ions) has a significant negative impact on the production and quality of struvite. The authors also observed that when SHWs were treated with a negligible concentration of Ca²⁺ (molar ratio of Mg²⁺/Ca²⁺ > 20), 80% of total phosphorus was removed via struvite precipitation. Also, higher rates of nitrogen and phosphorus removal were obtained at pH 9.5 with a 2:1 Mg²⁺/PO₄³⁻ molar ratio. Sreyvich et al. (2020) also evaluated SHWs for nutrient recovery and concluded that this residue is promising for struvite recovery by obtaining 99.3% phosphate and 98.1% ammonium removal using a PO₄³⁻/Mg²⁺ molar ratio of 1:3 at pH 9.0.

In addition to SWs and SHWs, DWs are also commonly investigated for struvite recovery due to their high concentrations of nitrogen and phosphorus (Rabinovich et al., 2018; Lavanya and Thanga, 2020). However, DWs have high concentrations of Ca^{2+} ions, which prompts many researchers to study techniques and operational strategies aimed at optimizing struvite recovery through the use of this AWW as a substrate (Numviyimana et al., 2020).

Thus, another possibility is the recovery of phosphorus from hydroxyapatite precipitation. Hydroxyapatite is used in the medical and dental fields as a coating material for metal implants and for filling bone cavities (Valente, 1999). Ease of handling and low cost of inputs are considered the main advantages of recovering this mineral from AWWs (De-Bashan and Bashan, 2004). However, compared to struvite, hydroxyapatite has no potential as a fertilizer for agriculture due to its low solubility and sufficient Ca^{2+}/P specific binding strength to hinder P availability in the soil (Hao et al., 2013; Shashvatt et al., 2018; Li et al., 2020).

DWs are promising for the recovery of phosphorus via hydroxyapatite precipitation since they commonly have high concentrations of phosphate, ammonium and calcium (up to $950 \text{ mg L}^{-1} \text{ Ca}^{2+}$) (Demirel et al., 2005; Kharbanda and Prasanna, 2016). Generally, calcium salts are used during the production of dairy products, which could decrease costs by supplementing this compound in hydroxyapatite recovery (Karadag et al., 2015).

Production of algal biomass, bacterial biomass and products derived from biological treatment of agricultural and agro-industrial wastewaters

Besides prospecting for nutrients, a diversity of bioproducts can be recovered through biological treatments in aerobic processes. Among these products, algal biomass, bacterial biomass and products derived from aerobic treatment stand out (Wang et al., 2015; Lu et al., 2019). Aerobic treatment is an oxidation process by which microorganisms degrade organic matter and other pollutants in the presence of oxygen (O_2). In this type of treatment, the main objective is to achieve a high degree of substrate conversion. One of the fundamental advantages is that the oxidative degradation of carbon present in wastewater provides the necessary energy to propagate microorganisms that act as catalysts. (Ranade and Bhandari, 2014). For this reason, biological treatment in aerobic AWW processes has been studied to obtain biomass to extract cellular components that may be useful industrially, such as carbohydrates, proteins, lipids and enzymes.

Wang et al. (2015), for example, studied the treatment of SWs at different dilutions (without dilution and dilutions of 5, 10 and 20 times), using the microalga *Chlorella vulgaris* JSC-6 in a photobioreactor to obtain biomass rich in carbohydrates, which can be used as a raw material for the fermentative production of biofuels. The authors achieved about 60–70% removal of COD and 40–90% removal of N-NH_3 depending on the dilution rate adopted, with the highest removal rate ob-

tained at 20 times dilution. Mixotrophic cultivation using wastewater diluted five times resulted in the highest biomass concentration (3.96 g L^{-1}). Besides, the carbohydrate content in microalgae produced from the SWs can reach 58% (dry weight).

Lu et al. (2019) investigated photosynthetic bacteria's use to treat BWs in a photosynthetic bacterial-membrane bioreactor (PS-MBR) on a pilot scale, aimed at the production of bacterial biomass rich in compounds of industrial interest. The authors obtained satisfactory results, reaching COD removal above 97% and yields of biomass, proteins, polysaccharides, carotenoids, bacteriochlorophyll and coenzyme Q10 of respectively 0.51, 0.21, 0.089, 0.0013, 0.0054 and $0.019 \text{ g g}^{-1} \text{ COD}$ removed. These bioproducts are added value compounds that can be used in agriculture and the cosmetic and medical industries.

Methane and hydrogen production from anaerobic treatment of agricultural and agro-industrial wastewaters

Another biological treatment option for AWWs is anaerobic treatment, which is more complex than aerobic treatment due to the different metabolic pathways that microorganisms can use to degrade organic matter present in waste. In recent years, this type of treatment's relevance has increased due to higher energy costs and the operational and managerial problems of aerobic processes, such as excessive sludge disposal (Show and Lee, 2017).

Conventionally, anaerobic digestion has been adopted for the production of bioenergy from different organic residues, mainly for CH_4 prospecting, which can be used for the generation of electricity, heat, steam, as a vehicle fuel and for injection into the natural gas network for domestic use, as well as for the production of H_2 , which can be used as fuel in vehicles and for electricity generation (Silva et al., 2020a). CH_4 is the biogas purification product, that is, the removal of impurities present, such as CO_2 , water, H_2S and siloxanes. The main technologies used for this purpose are pressure swing adsorption, high-pressure water washing, organic solvent washing, amine clearance, membrane separation and cryogenic separation (Khan et al., 2017). This stage is considered the most expensive in the CH_4 production and recovery process. Therefore, it is crucial to adopt the most effective and efficient technology to obtain the required degree of purity for a specific application (Muñoz et al., 2015).

When considering the viability of waste as a raw material for a biogas generation plant, it is necessary to understand how the production of CH_4 or H_2 occurs from this substrate (Alzate et al., 2012). For this, the biogas potential production (BPP) test is widely used, and as the experimental conditions of this test are not yet fully standardized, it is possible to adapt it to evaluate different substrates, inoculants and gases, mainly CH_4 and H_2 (Strömberg et al., 2014). The BPP test results mostly in stoichiometric coefficients of biogas production and cell growth, which can be used to estimate the gas of interest and manage the sludge produced in anaerobic treatment units (Sun et al., 2015).

The technical literature presents research on the BPP for each of the AWWs analyzed in this work, showing that these substrates have potential for prospecting this bioproduct (Table 3). As an example, Yang et al. (2016) studied the production of CH_4 in an anaerobic sequential batch reactor (ASBR) using SWs as substrate. They reported that the highest volumetric methane production rate ($1.95 \text{ L L}^{-1} \text{ d}^{-1} \text{ CH}_4$) was obtained when the system was operated at 35°C with an organic load of $7.2 \text{ g L}^{-1} \text{ d}^{-1} \text{ VS}$. Enitan et al. (2018) reported that 80% of the organic matter used from the BWs was converted to CH_4 in an upflow anaerobic sludge blanket — UASB reactor.

Martí-Herrero et al. (2018) investigated the production of biogas treating SHWs in tubular anaerobic digesters, aiming to identify the best operational conditions for its production. The organic loading rate (OLR) varied from 0.04 to $1.13 \text{ kg m}^{-3} \text{ d}^{-1} \text{ VS}$ and the hydraulic detention time (HDT) from 3.2 to 87.4 days. The authors observed a peak of biogas production of $0.2 \text{ m}^3 \text{ m}^{-3} \text{ d}^{-1}$ for OLR of $0.37 \text{ kg m}^{-3} \text{ d}^{-1} \text{ SV}$ with 9.7 days HDT. COD removal above 70% was achieved with HDT greater than 19 days.

Regarding the production of H_2 , Silva, A.N. et al. (2019) evaluated the effect of OLR on H_2 production from the use of DWs as a substrate in an anaerobic fluidized-bed reactor (AFBR). Different OLRs of 28.7, 53.2 and $101.7 \text{ kg m}^{-3} \text{ d}^{-1} \text{ COD}$ and different HDT corresponding to 8, 6 and 4 h, respectively, were applied. The researchers concluded that the increase in OLR negatively affects the production of H_2 since the gas yield fell from 2.56 ± 0.62 to $0.95 \pm 0.28 \text{ mol H}_2$ per mol of carbohydrate as OLR increased from 28.65 to $95.76 \text{ kg m}^{-3} \text{ d}^{-1} \text{ COD}$. The content of H_2 in biogas and the highest volumetric production of H_2 were respectively $35.72 \pm 9.43\%$ and $0.80 \pm 0.21 \text{ L h}^{-1} \text{ L}^{-1} \text{ H}_2$ when the OLR was $53.25 \pm 7.81 \text{ kg m}^{-3} \text{ d}^{-1} \text{ COD}$. Sittijunda and Reungsang (2017) evaluated the production of H_2 from RG and found a maximum productivity rate of $3.2 \text{ L L}^{-1} \text{ d}^{-1} \text{ H}_2$, but the COD removal efficiency was not presented.

Despite extensive research on the anaerobic digestion of AWWs and on the prospecting and purification of biogas, the use of CH_4 in Brazil from landfills and sewage treatment plants (STPs) was only regulated in 2017 by the National Petroleum Agency, Natural Gas and Biofuels (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis — ANP) with ANP Resolution No. 685/2017, which promoted an increase in the share of this resource in the Brazilian energy matrix (ANP, 2017). According to the International Center for Renewable Energies-Biogas (Centro Internacional de Energias Renováveis-Biogás — CIBiogás) between 2010 and 2018, the share of biogas in the Brazilian energy matrix increased from 0.01%, (14 thousand toes, a ton of oil equivalent) to 0.07% (CIBiogás, 2020). In 2018, the primary sources of biogas production were landfills (72%), the food/beverage industries (14%), swine farming (7%) and sewage sludge (5%) (EPE, 2019). Thus, the importance of STPs and agribusiness for consolidating a market for biogas and CH_4 is perceived. Nonetheless, Brazil still has an underutilized potential, having only 275 biogas production plants

in operation, mostly located in Brazil's South and Southeast regions (CIBiogás, 2020).

Production of carboxylic acids from anaerobic treatment of agricultural and agro-industrial wastewaters

There has been a trend in the search for by-products from the acidogenic fermentation stage of anaerobic digestion, such as short-chain carboxylic acids (SCCAs) (acetic acid – C2, propionic – C3, butyric – C4, and valeric – C5). These compounds are building block chemicals widely applied in the industry in producing varnishes, paints, perfumes, disinfectants, surfactants, textile auxiliaries, medicines and food products (Lee et al., 2014). The organic production of carboxylic acids (CAs) has been advocated as an effective way to generate sustainable fuels and chemicals from biomass and organic waste (Silva et al., 2020b). Conventionally, CAs are produced by petrochemical routes, and for this reason, their production by biological means from substrates rich in organic matter, as is the case of AWWs, is interesting both from an environmental and economic point of view (Sittijunda and Reungsang, 2017).

The biological production of CAs occurs during the hydrolytic-acidogenic process of organic matter, requiring the inhibition of the methanogenesis and sulfate reduction steps to block the conversion of CAs to CH_4 and H_2S (Kleerebezem et al., 2015). The main strategies for inhibiting the activity of methanogenic archaea and sulfate-reducing bacteria are the addition of chloroform, which acts by inhibiting the coenzyme M reductase necessary for the metabolism of archaea (Viñana et al., 2019), the addition of 2-bromoethanesulfonic acid (2-BES), which acts in the inhibition of the acetyl-CoA route, and the combined addition of chloroform and molybdate, which works directly in the enzymatic inactivation. However, the use of chemical agents in this inhibition increases the production of CAs, which encourages the development of studies related to other inhibition strategies, such as pH reduction and nutritional restriction (Siriwongrungron et al., 2007; Ge et al., 2015).

SCCAs are the main products of acidogenic fermentation of organic residues, while medium-chain carboxylic acids (MCCAs), which have six to twelve carbon atoms, are formed in lower concentrations (Steinbusch et al., 2011). MCCCAs are formed during the carboxylic chain elongation process (CCEP), in which an SCCA such as C2 reacts with reduced organic material, usually ethanol or other alcohol, forming an MCCA such as caproic acid (C6) and caprylic acid (C8) (Cavalcante et al., 2017).

MCCAs are more economically attractive than SCCAs and can be used as food additives, antimicrobial agents, precursors for biodiesel production, and bioplastics production (Strazzera et al., 2018). In addition to greater industrial applicability, MCCAs are easier to extract from the reaction medium compared to SCCAs because of their greater hydrophobicity, reducing costs with downstream processing of these bioproducts (Grootscholten et al., 2013). It is estimated that the aggre-

gate value of MCCAs is 2,000–2,500 USD ton⁻¹, thus being higher than the market price of SCCAs (400–2,500 USD ton⁻¹), CH₄ (200–600 USD ton⁻¹) and H₂ (800–1,600 USD ton⁻¹) (Bastidas-Oyanedel et al., 2015; Moscoviz et al., 2018; Silva et al., 2020a).

In this sense, studies indicate that the recovery of CAs from the acidogenic fermentation of agricultural and agro-industrial waste is possibly more advantageous in economic terms than CH₄ and H₂ (Bastidas-Oyanedel and Schmidt, 2018). Silva et al. (2020a) reported that the gross added value of CAs is higher than that of CH₄ and H₂. However, it is necessary to carry out further economic studies, mainly involving the analysis of downstream processing costs (e.g., costs involved in extracting CAs from the fermentation medium).

Morais et al. (2020a) and Coelho et al. (2020b) assessed the CA production potential of SWs and DWs, respectively. The experiments were carried out in four batch reactors made of borosilicate glass with a reaction volume of 250 and 50 mL of headspace, inoculated with the brewery sludge at a substrate/inoculum (S/I) of 0.60 ± 0.04 g COD per g SSV. To inhibit methanogenic activity, the authors added chloroform 0.05% (v/v) to the basal medium. Morais et al. (2020a) reported that 40% of the applied organic matter from SWs was bio-converted to CAs, with a yield of 0.33 g acids per g COD. Coelho et al. (2020b) observed that DWs have a high potential for acidification under acidogenic conditions and obtained the conversion of 83% of the COD applied to CAs, representing a yield of 0.66 g acids per g COD. The leading CAs formed were C2 and C4; however, the authors pointed out that SWs and DWs have the potential for the production of MCCAs because even without the addition of electron donors or the application of other methods to enhance CCEP, C6 was formed in low concentrations.

In further research, Morais et al. (2021) and Coelho et al. (2020a) also evaluated the prospecting of CAs from SHWs and RG, respectively, using the same operational conditions as their previous studies with SWs and DWs. For SHWs, the authors reported the conversion of 76% of COD to CAs (yield of 0.55 g acids per g COD), while for RG a yield of 0.62 g acids per g COD was obtained, corresponding to 82% conversion of applied organic matter.

On the basis of these studies, the authors concluded that more soluble AWWs generally have a greater potential for CA production due to the reduction of the hydrolysis step and the fact that organic matter is readily available for acidogenic microorganisms, which promotes rapid use and bioconversion of the substrate into CAs. In this sense, SHWs, DWs, BWs and RG because of their high levels of soluble organic matter are more promising substrates to be investigated for the production of CAs than substrates that have a higher concentration of organic matter in the particulate fraction, such as SWs. In this perspective, showing the high potential of soluble substrates for the organic production of CAs, Yin et al. (2016) investigated the acidogenic fermentation of glucose, peptone and RG in batch reactors inoculated with mixed biomass from a brewery wastewater treatment. They re-

ported average yields of 0.66, 0.60 and 0.51 g COD per g COD for these substrates, respectively.

To increase the production of MCCAs in acidogenic processes and to enhance, several strategies have been investigated, such as the establishment of optimized operational parameters (pH, temperature, volumetric organic load, hydraulic detention time) and the external addition of donors of electrons to the fermentation process (Steinbusch et al., 2011). Approximately 80% of studies aimed at producing C6 use ethanol as an electron donor to favor CCEP. However, this external addition can cause environmental impacts and increase the costs of the fermentation process. Therefore, one of the focuses of current research is to optimize ethanol's dose required by CCEP (Moscoviz et al., 2018).

Another technique to favor CCEP is bio-augmentation (addition of microorganisms specialized in chain extension to mixed microbial cultures). According to Hung et al. (2011), bio-augmentation can improve the rate of degradation of complex compounds by combining microorganisms' metabolic pathways and assisting in producing precursors (C2 and C4) for CCEP. Dams et al. (2018) conducted a C6 production experiment in batch reactors by the RG's acidogenic fermentation using bio-increased brewing sludge with *Clostridium acetobutylicum* ATCC 824 as an inoculum and adding 100 mM ethanol to stimulate CCEP. The authors reported that the C6 concentration increased from 1.61 to 3.82 g L⁻¹.

Another resource studied to increase the production of MCCAs in anaerobic reactors is the extraction concomitant with its output. This process reduces problems of inhibition of microbial activity due to the toxicity of the CAs formed. The production of CAs in anaerobic reactors requires extraction techniques specific to the type of acid produced. Usually, a selective extraction module for only one MCCA is the preferable choice to relieve toxicity to microorganisms of this product and recirculate to the reactor the remaining SCCAs not yet elongated to be reused in the process (Cavalcante et al., 2017).

Hybrid membrane modules with extracting liquids have been among the leading technologies for prospecting CAs (Moraes et al., 2015). In this process, the more hydrophobic CA in greater concentration has removal priority (Ge et al., 2015). Although there are several techniques capable of extracting CAs from anaerobic fermentation processes, including ion exchange resin, electrodialysis and liquid-liquid extraction membrane, the recovery of these bioproducts from the reaction (fermented) liquid is still one of the main barriers of the biological process production of CAs, requiring further studies on the optimization of operational parameters (López-Garzón and Straathof, 2014).

Conclusion

On the basis of the technical literature review carried out on the composition and physical-chemical characterization of agricultural and agro-industrial wastewaters (AWWs), it was possible to conclude

that swine wastewaters (SWs), slaughterhouse wastewaters (SHWs) and wastewaters from milk processing (DWs) are the most promising for the recovery of struvite since they generally have high levels of phosphorus and nitrogen. DWs also stand out for the recovery of hydroxyapatite due to high concentrations of phosphorus and calcium. SWs and wastewaters from beer production (BW) are commonly used in research to recover biomass rich in carbohydrates, proteins and polysaccharides. All the AWWs analyzed are suitable for prospecting

for biogas, methane and hydrogen. The more soluble AWWs (e.g., SHWs, DWs, BWs and residual glycerol — RG) are more promising for research in producing carboxylic acids compared to more particulate substrates, such as SWs. The scarcity of studies with fruit processing wastewaters (FPWs) from ice cream production is noteworthy. Thus, due to the high output of AWWs, Brazil is a promising country for the implementation of treatment plants that aim to recover resources from these liquid wastes.

Contribution of authors:

Morais, N.W.S.: Conceptualization, methodology, validation, formal analysis, investigation, data curation, writing - original draft, and writing — review and editing. Coelho, M.M.H.: Conceptualization, methodology, validation, formal analysis, investigation, data curation, writing — original draft, and writing — review and editing. Sousa e Silva, A.: Methodology and writing — review and editing. Pereira, E.L.: Conceptualization, methodology, supervision, validation and acquisition of funding.

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