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Xylose a carbon source for the production of biosurfactant: mini review

Xilose uma fonte de carbono para produção de biossurfactante: mini revisão

La xilosa, una fuente de carbono para la producción de biosurfactantes: mini revisión

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Maria dos Remédios Araújo Vieira Neta
ORCID: https://orcid.org/0000-0003-0788-1579
Federal University of São Carlos, Brazil
E-mail: remediosneta@gmail.com
Mariana Amaral Azevedo
ORCID: https://orcid.org/0000-0002-1682-8967
Federal University of São Carlos, Brazil
E-mail: marianaaz2009@hotmail.com
Tiago Palladino Delforno
ORCID: https://orcid.org/0000-0002-1705-0763
Federal University of São Carlos, Brazil
E-mail: palladino@alumni.usp.br
Iolanda Cristina Silveira Duarte
ORCID: https://orcid.org/0000-0002-9141-1010
Federal University of São Carlos, Brazil
E-mail: iolanda@ufscar.com

Abstract
Xylose is the second most abundant monosaccharide in nature. Xylose monomers are part of the structure of hemicellulose, which shows amorphous structure and is easily degraded by acid hydrolysis. Xylose is widely studied for xylitol and biofuels production; however, it is still little explored for the production of biosurfactants, which are active surface molecules with emulsifying properties, are biodegradable and are non-toxic to the environment. Bacteria, fungi and yeasts are extensively studied for the production of biosurfactants from different carbohydrates, oils and hydrocarbons, but there are few reports in the literature about the production of biosurfactants from hemicellulosic hydrolysates rich in xylose. Some studies show that bacteria and yeasts generally produce glycolipids from hemicellulosic hydrolysates. Due to the different properties of glycolipids, they can be used in different areas of industry, as they can be applied as bioremediators, bioinsecticides and antimicrobials.
Keywords: Sugars; Hemicellulose; Microorganisms; Hydrolysates; Biological surfactants.

Resumo
A xilose é o segundo monossacarídeo mais abundante na natureza. Os monômeros de xilose fazem parte da estrutura da hemicelulose, que apresenta estrutura amorfa e é facilmente degradada pela hidrólise ácida. A xilose é bastante estudada para produção de xilitol e biocombustíveis, no entanto, ainda é pouco explorada para produção de biossurfactantes, que são moléculas de superfície ativa com propriedades emulsificantes, biodegradáveis e não são tóxicos ao ambiente. Bactérias, fungos e leveduras são bastante estudados para produção de biossurfactantes a partir de diferentes carboidratos, óleos e hidrocarbonetos, mas há poucos relatos na literatura sobre a produção de biossurfactantes a partir de hidrolisados hemicelulósicos ricos em xilose. Alguns trabalhos mostram que bactérias e leveduras geralmente produzem glicolipídios a partir de hidrolisados hemicelulósicos. Devido as diferentes propriedades dos glicolipídios estes podem ser empregados em diferentes áreas da indústria, pois podem ser aplicados como biorremediadores, bioinseticidas e antimicrobianos.
Palavras-chave: Açúcares; Hemicelulose; Microrganismos; Hidrolisados; Tensoativos biológicos.

Resumen
La xilosa es el segundo monosacárido más abundante en la naturaleza. Los monómeros de xilosa forman parte de la estructura de la hemicelulosa, que tiene una estructura amorfa y se degrada fácilmente por hidrólisis ácida. La xilosa está ampliamente estudiada para la producción de xilitol y biocombustibles, sin embargo, todavía se explora poco para la producción de biosurfactantes, que son moléculas de superficie activa con propiedades emulsionantes, biodegradables y no tóxicas para el medio ambiente. Las bacterias, hongos y levaduras se estudian ampliamente para la producción de biosurfactantes a partir de diferentes carbohidratos, aceites e hidrocarburos, pero hay pocos informes en la literatura sobre la producción de biosurfactantes a partir de hidrolizados hemicelulósicos ricos en xilosa. Algunos estudios muestran que las bacterias y las levaduras generalmente producen glicolípidos a partir de hidrolizados hemicelulósicos. Por las diferentes propiedades de los glicolípidos se pueden utilizar en diferentes áreas de la industria, ya que se pueden aplicar como biorremediadores, bioinsecticidas y antimicrobianos.
Palabras clave: Azúcares; Hemicelulosa; Microorganismos; Hidrolizados; Tensioactivos biológicos.

1. Introduction

Among the sugars that make up the structure of hemicellulose, xylose (pentose with 5 carbon atoms) is one of the main sugars (Resende et al., 2017; Harahap, 2020), presenting molecular formula $C_5H_{10}O_5$; in addition, it is the second most abundant sugar derived from lignocellulosic biomass after glucose ($C_6H_{12}O_6$) (Chen 2017; Resende et al., 2017; Silva et al., 2010).

The use of hemicellulosic hydrolysates, rich in pentoses, represents a sustainable way to recycle lignocellulosic biomasses, which are residues of large-scale agroindustrial production. Techniques for converting lignocelluloses into xylose are widespread (Harahap, 2020) and, in the last years, fermentation processes that use xylose as a feedstock have been receiving a broad attention from industries due to xylose being easily obtained in large quantities and it can also be converted in xylitol and ethanol by microorganisms during fermentation processes (Ahuja et al., 2020; Cheng et al., 2011; Fan et al., 2020; Rodrussamee, Sattayawat & Yamada, 2018; Tamburini et al., 2019; Vilela et al., 2015).

As there are few reports in the literature about the ability of microorganisms to convert xylose into metabolites with surfactant capacity (Cortés-Camargo et al., 2016; Chen et al., 2019; Jain et al., 2013; Joshi-Navare, Singh & Prabhune, 2014; Konishi, Yoshida & Horiuchi, 2015; Moldes et al., 2013; Panjiar et al., 2020; Portilla-Rivera et al., 2009), this review aimed to exclusively discuss about obtaining hemicellulosic hydrolysates rich in xylose, for the production of biosurfactants by bacteria and yeasts.

2. Methodology

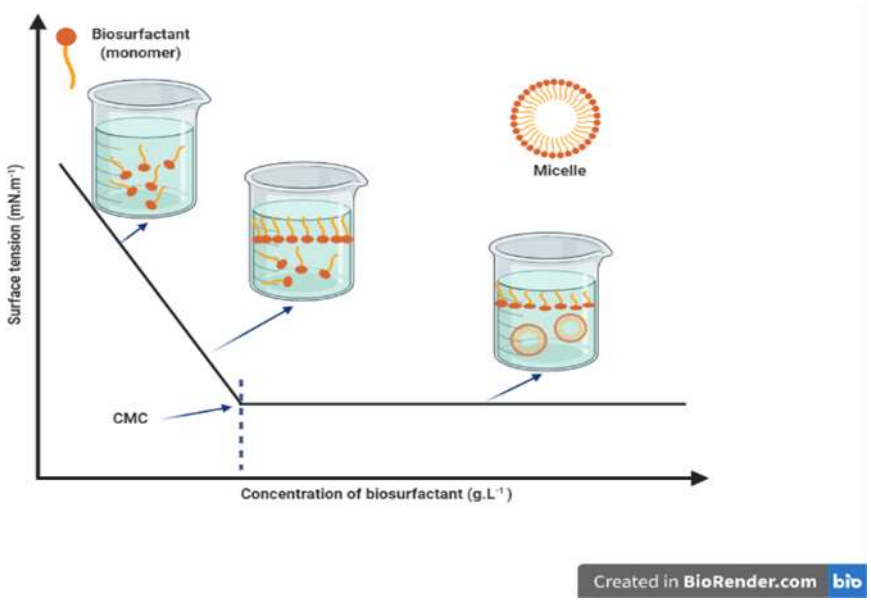
This study is a literature review on the use of lignocellulosic biomass, rich in xylose for the production of biosurfactant by microorganisms. The review covers articles and scientific books available in the indexing databases: Scielo (Scientific Eletronic Library Online), Google Scholar, ScienceDirect, PubMed and Wiley Online Library. The search for articles in the different databases used different terms such as: biosurfactants, microbial surfactants, biological surfactants, lignocellulosic biomass, lignocellulose, agroindustrial waste, acid hydrolysis, acid or chemical treatment, carbon source (xylose). There was no time cut for the choice of articles used in this study.

3. Biosurfactants: Surfactants of Biological Origin

Microorganisms such as bacteria, fungi and yeasts can synthesize active surface and emulsifying properties molecules, called biosurfactants (Chen et al., 2019; Hu et al., 2020; Marcelino et al., 2019). Biosurfactants are compounds of an amphiphilic nature containing a hydrophilic and a hydrophobic group referred to as head and tail, respectively. One of the main biosurfactants properties is the reduction of the surface tension (ST) and interfacial tension (IT) among different phases (liquid-air, liquid-liquid) and increased solubility of immiscible compounds (Akbari et al., 2018). A biosurfactant is considered effective when it reduces the ST of the water from 72 $mN.m^{-1}$ to values equal to or less than 40 $mN.m^{-1}$ (Cortés-Camargo et al., 2016; Haba et al., 2000; Joshi-Navare, Singh & Prabhune, 2014; Panjiar et al., 2020), and it reduces the IT between liquids with different degrees of polarity, as between water and hexadecane, from 40 $mN.m^{-1}$ to 1 $mN.m^{-1}$ (Mulligan, 2005).

The efficiency of biosurfactants can be measured through the critical micellar concentration (CMC). The best biosurfactants have a CMC of less than 200 $mg.L^{-1}$ (Ashish, 2018; Cortés-Camargo et al., 2016; Nogueira Felix et al., 2019). The CMC is the lowest surfactant concentration required for maximum ST reduction; when CMC is reached, the monomers of the biosurfactants associate forming the micelles, vesicles or lamellae and, from the micelles formation, the ST will remain constant or the change will be very small (Figure 1) (Nguyen et al., 2008; Whang et al., 2008). The CMC is influenced by the solvent's pH, temperature and ionic strength (Akbari et al., 2018; Mulligan, 2005; Santos et al., 2016; Sharma, 2016).

Figure 1. Relationship between the biosurfactant concentration ($g.L^{-1}$), surface tension ($mN.m^{-1}$) and micelle formation, created with BioRender.com.



Source: Authors.

Biosurfactants also have the ability to form stable emulsions for up to 24 hours or more (Marcelino et al., 2019; Panjiar et al., 2020; Willumsen e Karlson, 1996). The emulsification is formed when the surfactant accumulates between phases and it decreases ST and IT, forming the emulsion (Akbari et al., 2018). Another important biosurfactants' property is biodegradability, for they are easily degraded by microorganisms present in the environment, and they have low toxicity, unlike synthetic surfactants that are derived from petroleum and are difficult to break down, then can cause environmental pollution (Sharma, 2016).

As biosurfactants are biodegradable and have low toxicity, they become an alternative over their chemical homologues, and they are of interest for applications in many areas of the industry (food, pharmaceutical and cosmetics) and environment (bioremediation) (Akbari et al., 2018; Ashish, 2018; Santos et al., 2016; Sharma, 2016).

The biosurfactants are characterized according to their microbial origin and chemical nature, and they can be classified by the size of the molecules, leading to a classification of low and high molecular weight biosurfactants (Table 1). Glycolipid-type biosurfactants (ramnolipids, soforolipids (SLs), trehalolipids and lipids of mannosileritritol (MEL)), lipopeptides (surfactin) and polymeric surfactants (emulsan) are extensively studied.

One of the main characteristics of ramnolipids is the ability to reduce ST to values of 29 $mN.m^{-1}$; this biosurfactant is mainly produced by *Pseudomonas aeruginosa* from various substrates such as alkanes, pyruvate, citrates, sugars and oils. Many studies investigate the ramnolipids' ability to biodegrade petroleum hydrocarbons (Haba et al., 2000; Nguyen et al., 2008; Santos et al., 2016). The SLs are mainly produced by yeasts from to the genus *Candida* (Faria et al., 2014; Kurtzman et al., 2010; Samad et al., 2014); SLs can reduce ST to approximately 33 $mN.m^{-1}$ and IT between *n*-hexadecane and water from 40 to 5 $mN.m^{-1}$ (Banat et al., 2015).

MELs are promising biosurfactants due to their antitumor activity, and they can be used treatments for microbial infections (Arutchelvi et al., 2008). They are synthesized by species of the *Pseudozyma* genus on oily substrates and sugars (Faria et al., 2014; Lang, 2002). Trehalolipids are synthesized by species of *Mycobacterium*, *Nocardia*, *Corynebacterium*, *Arthrobacter* spp. and *Rhodococcus* genera (Vijayakuma & Saravanan, 2015). However, the fungus *Fusarium fujikuroi* recently showed the ability to synthesize this biosurfactant with the capacity to reduce ST from 70 $mN.m^{-1}$ to 20 $mN.m^{-1}$ (Reis et al., 2018).

Table 1. Biosurfactants classification and producing microorganisms.

	Class	Type	Microorganism	References
Low molecular weight	Fatty acid		*Corynebacterium lepus*	Cooper, Zajic & Gerson (1979)
	Neutral lipids		*Nocardia erythropolis*	Macdonald, Cooper & Zajic (1981)
	Phospholipids		*Klebsiella pneumoniae*	Nwaguma, Chikere & Okpokwasili (2016)
	Glycolipids	Ramnolipids	*Pseudomonas aeruginosa*	Dobler et al. (2017)
		Soforolipids	*Candida bombicola*	Samad et al. (2014)
		Trealolipids	*Rhodococcus erythropolis*	Peng et al. (2007)
		Mannosilitritol lipids	*Pseudozyma (Candida) antarctica*	Faria et al. (2014)
	Lipopeptides and Lipoproteins	Surfactin	*C. tropicalis*	Ashish (2018)
			B. subtilis	Nogueira Felix et al. (2019)
				Freire et al. (2020)
High molecular weight	Polymeric surfactants	Emulsan	*Acinetobacter calcoaceticus*	Amani & Kariminezhad (2016)
		Liposan	*C. lipolytica*	Cirigliano & Carman (1984)
		Biodispersan	*A. calcoaceticus*	Shabtai (1990)
		Yansan	*Yarrowia lipolytica*	Amaral et al. (2006)
		Manana-lipid-protein	*P. aeruginosa*	Käppeli et al. (1984)

Source: The table was structured by the authors from the compilation of different articles available in the literature.

Surfactin is mainly produced by *Bacillus subtilis*; this biosurfactant is fairly studied for it shows high surface activity. With a10^{-5} m CMC, it reduces the ST to 27 mN.m^{-1} (Chen et al., 2015). In addition, surfactin has antimicrobial and antifungal activity (Chen et al., 2015; Chen et al., 2019; Hu et al., 2020; Whang et al., 2008; Willenbacher et al., 2015).

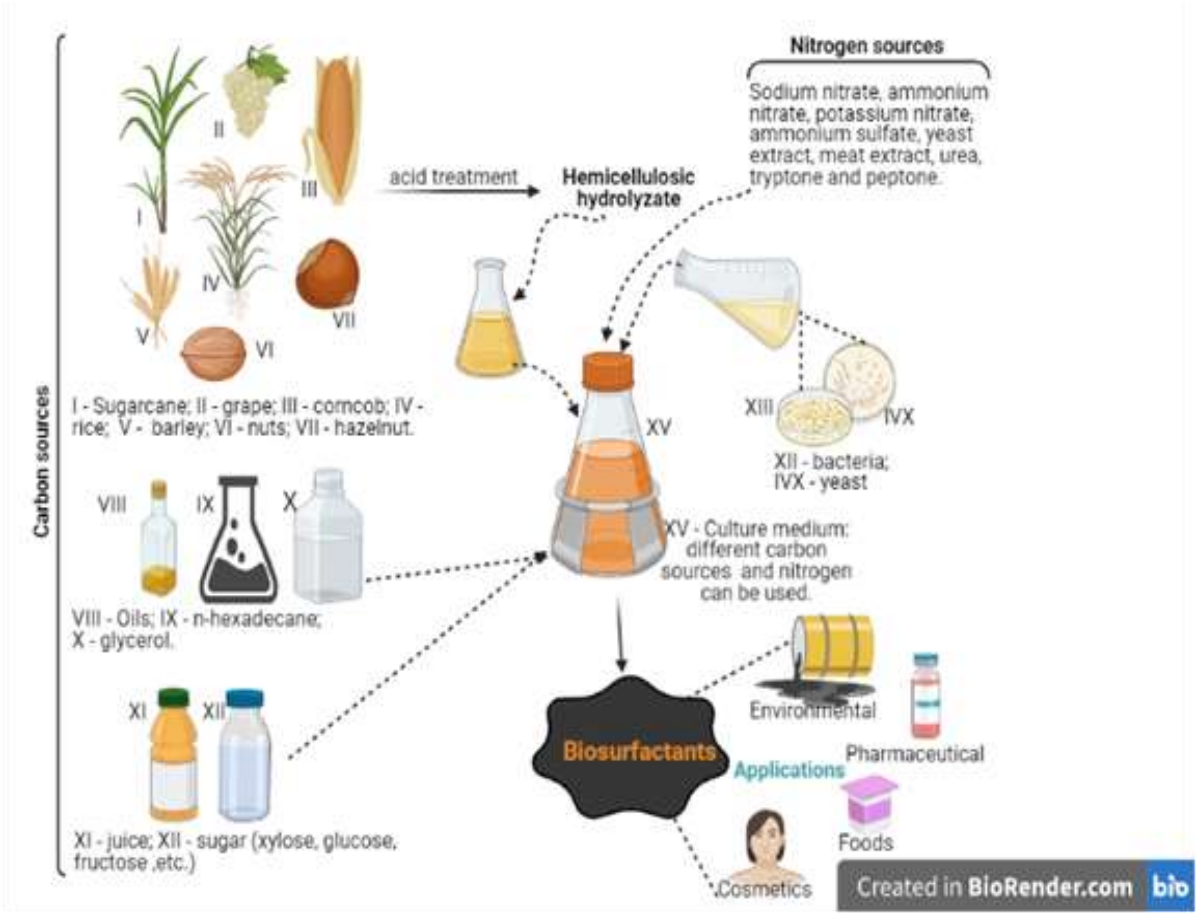
Emulsan is an emulsifier for hydro carbonates in water; it is produced mainly by strains of *Acinetobacter* (Amani & Kariminezhad, 2016; Santos et al., 2016). The CMC of 30 mg.L^{-1} of emulsan produced by *A. calcoaceticus* emulsifies 98% of petroleum and the ST and IT are reduced to 24 mN.m^{-1} e 3 mN.m^{-1}, respectively (Amani & Kariminezhad, 2016).

4. Importance of Carbon and Nitrogen Sources for the Production of Biosurfactants

The source of carbon and nitrogen play an important role in the biosurfactants' growth and production by microorganisms of various species. However, the required concentration of carbon and nitrogen varies from species to species (Archana, Tomar & Srinikethan, 2016; Haba et al., 2000; Hu et al., 2020; Konishi, Yoshida & Horiuchi, 2015; Santa Anna et al., 2002; Santos et al., 2016).

Different substrates can be used as a source of carbon for biosurfactants' production by microorganisms (Figure 2), such as hydrocarbons, carbohydrates, vegetable oils and oils from frying processes. In addition, industrial residues and lignocellulosic biomass, from agribusiness can also be used in the production of biosurfactants (Table 2). Many studies have had more attention on the lignocellulosic biomass' use (Hu et al., 2020; Marcelino et al., 2017; Marcelino et al., 2019; Panjiar et al., 2020; Moldes et al., 2007), that makes it possible the biosurfactants' production with up to 50% reduction in the price of the product, bearing in mind that biosurfactants do not compete with synthetic surfactants because the production value of the biosurfactants is expensive. Therefore, in order to conquer the market, to be commercialized and to compete with synthetic surfactants, biosurfactants must be produced at low cost.

Figure 2. Substrates used as a source of carbon and nitrogen for the biosurfactants' production by microorganisms, created with BioRender.com.



Source: Authors.

The most studied carbohydrate for biosurfactans' production is glucose both conventional and the one obtained from lignocellulosic biomass, but some studies are exploring xylose from lignocelluloses for the production of surfactants (Hu et al., 2020; Konishi, Yoshida & Horiuchi, 2015; Marcelino et al., 2017). However, during the the fermentation of hemicellulosic hydrolysates, which are composed of pentose and hexoses, glucose may inhibit the xylose metabolism either by suppression or by inactivation of the xylose transport system or catabolic enzymes (Portilla-Rivera et al., 2007), therefore, the rate of xylose assimilation by microorganisms becomes much slower than the rates of glucose assimilation (Osiro et al., 2018). In addition, few studies have shown that microorganisms such as yeasts, when grown in xylose, are very efficient in the production of secondary metabolites, however, they can be inhibited or decreased when the main carbon source is glucose (Kim et al., 2017; Panjiar et al., 2020; Turner et al., 2015).

Other studies have reported that catabolic repression may occur in biosurfactants production when glucose is used as the main carbon source (Cirigliano & Carman, 1984; Duvnjak, Cooper & Kosaric, 1982; Hauser & Karnovsky, 1954). In those, it was identified that, after almost finished glucose, the production of biosurfactants began to happen under stress conditions for *P. aeruginosa* cell. Ask et al., 2013; Banat et al., 1991 also observed that regarding xylose, the absorption rate did not dramatically decrease as to glucose.

Regarding nitrogen, in fermentative processes, when low nitrogen levels occur, bacterial growth can be limited, availing the production of metabolites. In contrast, excess nitrogen can limit the production of biosurfactants by inhibiting the microorganism's growth (Santos et al., 2016; Vigneshwaran, Vasantharaj & Sivasubramanian, 2016). The nitrogen sources used

for the production of biosurfactants by microorganisms can be organic or inorganic sources (Figure 2). In the scientific literature, there are reports of several salts such as sodium nitrate, ammonium nitrate, potassium nitrate and ammonium sulfate that are used as sources of inorganic nitrogen and yeast extract, meat extract, urea, tryptone and peptone are sources of organic nitrogen (Table 2) (Nurfarahin, Mohamed & Phang, 2018; Santos et al., 2016). The production of biosurfactants often occurs when nitrogen is depleted in the culture medium during the stationary cell phase (Nurfarahin, Mohamed & Phang, 2018).

Table 2. Carbon and nitrogen sources used for biosurfactants production by microorganisms.

Carbon	Nitrogen	Species	BS type	References
Hazelnut and walnut shells and distilled grape marc	Yeast extract, corn steep liquor	*Lactobacillus pentosus*	Nd	Portilla-Rivera et al. (2008)
Rice straw (hemicellulosic hydrolysate) Rice straw (enzymatic hydrolysate)	Soya hull, cotton seed oil cake, corn steep liquor, sodium nitrate, urea and ammonium sulfate	*Serratia nematodiphila*	Xylolipids	Panjiar et al. (2020)
N-hexadecane, paraffinic oil, glycerol and babassu oil	$NaNO_3$, $(NH_4)_2SO_4$ e CH_4N_2O	*Pseudomonas aeruginosa*	Ramnolipids	Santa Anna et al. (2002)
Glucose, glycerol, fructose and starch	Urea, yeast extract, ammonium chloride, peptone and ammonium nitrate	*P. aeruginosa* (MTCC 7815)	Nd	Archana, Tomar & Srinikethan (2016)
Corncob hydrolysate	Feather hydrolysate wastes and monosodium glutamate mill waste	*Bacillus subtilis* BS-37	Surfactin	Chen et al. (2019)
Hemicellulosic and cellulosic hydrolysate of vine-trimming shoots	$NaNO_3$, Na_2HPO_4 and yeast extract	*B. tequilensis* ZSB10	Nd	Cortés-Camargo et al. (2016)
D-xylose, D-glucose and de D-xylose/D-glucose mix	Sodium nitrate	*Pseudozyma antarctica* PYCC5048^T, *P. Aphidis* PYCC5535^T *e* *P. Rugulosa* PYCC5537^T	MEL	Faria et al. (2014)
Clarified cashew apple juice	$(NH_4)_2SO_4$ and Na_2HPO_4	*B. subtilis*	Surfactin	Nogueira Felix et al. (2019) Giro et al. (2009)
Waste frying oils	Yeast extract and $NaNO_3$	*P. aeruginosa* 47T2	Ramnolipids	Haba et al. (2000)
Corncob hydrolysate	Monosodium glutamate wastewater	*B. subtilis* 168	Surfactin	Hu et al. (2020)
Xylose and oleic acid	Sodium nitrate	*Pichia caribbica*	Xylolipid	Joshi-Navare, Singh & Prabhune (2014)
Corncob hydrolysate	Ammonium nitrate	*Starmerella bombicola* NBRC 1024	Sophorolipids	Konishi, Yoshida & Horiuchi (2015)
Sugarcane bagasse hemicellulosic hydrolysate	Yeast extract and ammonium nitrate	*Scheffersomyces stipites* NRRL Y-7124	Glycolipids	Marcelino et al. (2017)
Hemicellulosic hydrolysates from vineyard pruning waste	Yeast extract and corn steep liquor	*L. pentosus* CECT-4023^T	Glycoprotein / glycolipopeptide	Moldes et al. (2013)
Sucrose, dextrose, glycerol, fructose, starch and glucose	NH_4NO_3, peptone, yeast extract, asparagine, and urea	*Klebsiella pneumoniae* IVN51	Phospholipids	Nwaguma, Chikere & Okpokwasili (2016)

nd – non-determined, BS - biosurfactant.
Source: The table was structured by the authors from the compilation of different articles available in the literature.

5. Hydrolysis of Lignocellulosic Biomass and Production of Biosurfactant from Hemicellulosic Hydrolysates Rich in Xylose

Hemicellulose has an amorphous structure, with a linear chain showing ramifications and a lower degree of polymerization (~100-200); due to these characteristics, the structure of hemicellulose becomes easy to hydrolyze (Ahmad & Zakaria, 2019; Harahap, 2020; Lavarack, Griffin & Rodman, 2002).

The principle of the hydrolysis technique is to apply temperature and pressure to favor the acid penetration into the fibers, and then to release the monosaccharides present in the hemicellulose structure (Chen & Wang, 2017; Lavarack, Griffin & Rodman, 2002). Depolymerization of hemicellulose via acid hydrolysis is a commonly used way to solubilize monosaccharides (Harahap, 2020), xylose being the main monosaccharide produced; its production may vary from 75% to 90% in hydrolysates, and glucose and arabinose are produced to a lesser extent (Mussatto & Teixeira, 2010; Resende et al., 2017).

Depending on the conditions for hydrolyses processes, acetic acid may be produced and also sugar degradation products such as furfural and hydroxymethylfurfural (HMF) (Chen & Wang, 2017; Mussatto & Teixeira, 2010; Resende et al., 2017). The presence of these in hydrolysates can be toxic to the microorganisms' cellular metabolism during fermentative processes (Mussatto, Dragone & Roberto, 2005; Panjiar et al., 2020; Resende et al., 2017; Zhang et al., 2011). These compounds concentrations in the hydrolysates widely varies, depending on the conditions used for lignocellulosic biomass and the hydrolysis (Marcelino et al., 2019; Mussatto, Dragone & Roberto, 2005; Panjiar et al., 2020; Silva, Mussatto & Roberto, 2010).

The acids generated in the biomass hydrolysis are weak acids; however, because they are soluble in fats, the acids are able to cross the cell membrane of microorganisms, causing changes in pH and cytoplasm, thereby inhibiting microbial growth. Weak acids are generally used to preserve food (Chen & Wang, 2017). Acetic acid is formed when xylan acetyl groups are released (Harahap, 2020). Mussatto, Dragone & Roberto (2005) have demonstrated demonstrate that acetic acid concentrations higher than 3.0 $g.L^{-1}$ influence the production of xylitol by *Meyerozyma guilliermondii*; that acid concentration is highly toxic to yeast, but concentrations below that value did not affect yeast metabolism.

Furfural is usually formed in hydrolysates when xylose and arabinose degradation occurs, and HMF is formed if glucose is degraded (Mussatto, Dragone & Roberto, 2005; Roberto et al., 1991; Zhang et al., 2011). A recent study conducted by Panjiar et al. (2020) reported that *Serratia nematodiphila* also endures that concentration of acetic acid (3.0 $g.L^{-1}$), HMF and furfural present in rice straw hydrolysates used during fermentation to produce biosurfactant. It is evident that the inhibition of the cellular metabolism of microorganisms by the action of these compounds varies from species to species.

In other studies, that aimed to analyze the influence of by-products on the microorganisms' metabolism Cheng et al. (2011) demonstrated that the yeast *Candida maltosa* is able to metabolize both furfural and HMF, present in the xylose liquor. Zhang et al. (2011) also demonstrated that the yeast *Rhodotorula glutinis* is able to metabolize acetic acid and furfural when the carbon source xylose is present in the culture medium; however, in the presence of glucose these compounds inhibit yeast growth. Ask et al. (2013) also reported that the by-products furfural and HMF interfere in the absorption of sugars by *Saccharomyces cerevisiae*; in the presence of these compounds, the glucose absorption rate is highly reduced when compared to the xylose absorption rate.

Biological detoxification can be performed to remove furfural and HMF from hydrolysates (Cheng et al., 2011; Ran et al., 2014; Zhang et al., 2013); detoxification of hydrolysates with activated carbon can also be performed, which is usually the most used (Konishi, Yoshida & Horiuchi, 2015; Marcelino et al., 2019; Mussatto, Dragone & Roberto, 2005). However, the activated carbon's use may increase the total cost of production (Konishi, Yoshida & Horiuchi, 2015). Therefore, it is essential to control the conditions established in hydrolysis processes to minimize the concentrations of toxic compounds during the hemicellulose depolymerization.

The hydrolysis of hemicellulose with diluted acid, under mild treatment conditions, is proper for the production of xylose (Ji et al., 2017; Marcelino et al., 2019; Resende et al., 2017; Tian et al., 2017). Thermic treatment can be performed in high temperature (180 ºC) for a few minutes period (5 min) or at low temperature (120 ºC) for a 30 to 90 minutes period (Mussatto, Dragone & Roberto, 2005; Resende et al., 2017). But the most indicated process is the treatment with diluted acid and hydrolysis at low temperature (120 ºC), because under those conditions, the inhibitors are produced in a lower amount and xylose in a higher amount (Resende et al., 2017).

Diluted sulfuric acid (H_2SO_4) is commonly used to solubilize hemicellulose due to its low cost and high efficiency (Marcelino et al., 2019; Portilla-Rivera et al., 2008; Ji et al., 2017; Tian et al., 2017). Acids such as hydrochloric (HCl), nitric (HNO_3) and phosphoric (H_3PO_4) can also be used to degrade hemicellulose (Resende et al., 2017; Harahap, 2020). Other less corrosive acids, such as maleic and fumaric acid, can also be used for hemicellulose degradation, yet the efficiency of these acids in the hydrolysis process is lesser than the efficiency of sulfuric acid (Rusanen et al., 2017).

The hemicellulosic hydrolysates, resulting from the degeneration of hemicellulose fibers with acid, have a very acidic pH (pH 1,0) and, to be used in fermentation processes, the hydrolysates pH must be neutralized. The most used bases to adjust the pH are generally $CaCO_3$, NaOH, $Ca(OH)_2$ (Chen et al., 2019; Cortés-Camargo et al., 2016; Portilla-Rivera et al., 2008).

It is evident that different acids can be used to degrade hemicellulose fibers (Table 3), and the hydrolysates from this degradation are rich in fermentable sugars, in xylose mainly, which are currently being explored for biosurfactants production.

Table 3. Sugar concentration ($g.L^{-1}$) in lignocellulosic biomasses used for the production of biosurfactant, by different microorganisms.

Lignocellulosic biomass	**Sugar ($g.L^{-1}$)**			**Species**	**References**
	Xylose	**Glucose**	**Arabinose**		
Barley bran husks	40.7	5.82	7.47	*Lactobacillus pentosus*	Moldes et al. (2007)
Trimming vine shoots	19.1	9.18	2.81		
Corncobs	36.9	2.79	4.10		
Eucalyptus globulus chip	19.5	2.24	1.25		
Vineyard pruning	18.0	10.6	3.9		Moldes et al. (2013)
Distilled grape marc	8.2	2.2	2.1		Portilla-Rivera et al. (2008)
Hazelnut shells	20.0	0.6	0.6		
Walnut shells	18.4	1.3	1.6		
Sugarcane bagasse	58.76	3.67	4.30	*Cutaneotrichosporon mucoides*	Marcelino et al. (2019)
				Scheffersomyces stipitis	Marcelino et al. (2017)
Corncob	13.62	4.92	1.24	*Bacillus subtilis* 168	Hu et al. (2020)
	17.5	1.5	6.28	*B. subtilis* BS-37	Chen et al. (2019)
Rice straw	22.05	2.0	nd	*Serratia nematodiphila*	Panjiar et al. (2020)

nd – non-determined.
Source: The table was structured by the authors from the compilation of different articles available in the literature.

The probiotic bacterium *L. pentosus* ATCC-8041 was studied regarding the production of biosurfactants from distilled grape marc residue sugars and from hazelnut shells hydrolyzed (Portilla-Rivera et al., 2008), and in sugars of hemicellulosic hydrolysates from vineyard pruning (Portilla-Rivera et al., 2009). The first study shows that the biosurfactant from distilled grape marc and from hydrolyzed hazelnut shells emulsified 83% and 76.4% of kerosene, respectively. Emulsification is one of the properties that allow biosurfactants to be used in bioremediation processes in sites contaminated with hydrocarbons. In the second study, the substrate influenced the biosurfactant properties, since the glucose increasing, in the absence of xylose, produces a

biosurfactant with low surface activity. However, the combination of xylose and glucose 1.5 $g.L^{-1}$:3.5 $g.L^{-1}$, respectively, provides the best condition to produce the biosurfactant.

Moldes et al. (2011) have reported that as of hemicellulosic sugars, with a composition similar to vineyard pruning hydrolysates, supplemented with 10 $g.L^{-1}$ of yeast extract and 10 $g.L^{-1}$ of corn maceration liquor, *L. pentosus* has synthesized a biosurfactant with hydrocarbon degradation capacity. In 30 days, the biosurfactant degraded 76% of 7,0000 $mg.Kg^{-1}$ of the octane hydrocarbon in the soil. This result indicates that the biosurfactant produced by that bacterium can be used in bioremediation processes. That one biosurfactant was classified as glycoprotein (Moldes et al., 2013).

Low-cost waste such as barley bran husks, vineyard pruning, corncob and *Eucalyptus globulus chip* are rich in xylose and are promising for biosurfactant production by *L. pentosus*. In this study, Moldes et al. (2007) reported that the highest concentration of biosurfactant in $g.L^{-1}$ was obtained from hydrolysates of vineyard pruning (6.5 $g.L^{-1}$), reducing ST to 51 $mN.m^{-1}$, followed by corncob (4.7 $g.L^{-1}$), *E. globulus* detoxified hydrolysates (4.0 $g.L^{-1}$), and the lowest biosurfactant concentration was derived from barley bran husks hydrolysates (2.9 $g.L^{-1}$). The biosurfactants have reduced ST to 54, 55 and 56 $mN.m^{-1}$, respectively. According to the authors, the difference in the biosurfactant production may be related to the hydrolysates chemical composition, which varies between biomasses.

Using sugarcane bagasse hydrolysates composed of 40 $g.L^{-1}$, 2.7 $g.L^{-1}$ and 1.3 $g.L^{-1}$ of xylose, arabinose e glucose, respectively, Marcelino et al. (2017) reported a 0.70 $g.L^{-1}$ production of glycolipids by *Scheffersomyces stipitis* NRRL Y-7124. At the end of fermentation process (68h), yeast consumed 100% of glucose and 60% of xylose; the concentration of arabinose remained the same throughout the fermentation process, indicating that there was no consumption of this sugar. The produced glycolipid reduced ST to 52 $mN.m^{-1}$ and emulsified 70% of kerosene, in addition to presenting insecticidal activity, with 800 $mg.L^{-1}$ of glycolipids capable of destroying the exoskeleton of *Aedes aegypti* larvae in 12 hours, with an average lethal concentration (LC_{50}) estimated at 600 $mg.L^{-1}$. This result indicates that glycolipids can be used in formulations of larvicides used against neotropical disease vectors.

Marcelino et al. (2019) were able to produce SLs (11 $g.L^{-1}$) by *C. mucoides* UFMG-CM-Y6148 using hemicellulosic hydrolysates from sugarcane bagasse (58.76 $g.L^{-1}$ xylose; 4.33 $g.L^{-1}$ arabinose; 3.67 $g.L^{-1}$ glucose). In addition to the sugars in the hydrolysates, they had 2.4 $g.L^{-1}$ of acetic acid, 0.07 $g.L^{-1}$ of furfural and 0.15 $g.L^{-1}$ of HMF, these compounds concentration was less than 0.05 $g.L^{-1}$ after detoxification of hydrolysates with activated carbon; these compounds did not influence the yeast growth. In the fermentation process, after 25h and 96h, the glucose and xylose had already depleted, respectively. SL emulsified 65% kerosene and 51% vegetable oil, also exhibited stability under different pH, salinity and temperature conditions, but SL did not reduce ST and, according to the authors, the ionic force of water may have interfered. However, the biosurfactant stability is an important propriety so that biosurfactant can be used in industrial or environmental processes.

Some researchers combine hydrophilic and hydrophobic carbon sources to increase the biosurfactants production by microorganisms. Samad et al. (2014) used sorghum bagasse and corn fiber hydrolysates as a substrate for the production of biosurfactants by *C. (Starmerella) bombicola*, and they reached 3.6 $g.L^{-1}$ and 1.0 $g.L^{-1}$ of SLs, respectively. However, after the hydrolysates supplementation with 100 $g.L^{-1}$ of oil, the maximum production was of 84.6 $g.L^{-1}$ and 15.6 $g.L^{-1}$ of SLs, in the sorghum bagasse and corn fiber hydrolysates, respectively.

In a study conducted by Cortés-Camargo et al. (2016), it was shown that *B. tequelensis* ZSB10 presented capacity for growth and for production of 1.5 $g.L^{-1}$ of natural biosurfactant in culture medium containing 50% hemicellulosic hydrolysate and 50% cellulose hydrolysate stemming from hydrolysis with diluted acid, followed by enzymatic hydrolysis from vine-trimming wastes. The produced raw biosurfactant reduced ST to 38.6 $mN.m^{-1}$ and emulsified 47% of kerosene. When it comes to sugar consumption, after 52 hours of fermentation, glucose was depleted, while 57.63% of xylose was consumed in the same period of time. This shows that glucose is easily metabolized by microorganisms, influencing the xylose consumption.

Chen et al. (2019) reported that a wild strain of *B. subtilis* BS-37 produces surfactin at a concentration of 523 $mg.L^{-1}$, when grown in hydrolysates rich in xylose. However, Hu et al. (2020) demonstrated that the genetically modified *B. subtilis* 168 efficiently produced surfactin from the combination of a carbon source (commercial xylose) with nitrogen (tryptone), consuming 60% of 20 $g.L^{-1}$ xylose in 36 hours. In order to reduce production costs, the researchers replaced commercial xylose with corn cob hydrolysate (13.62 $g.L^{-1}$ xylose), combined to 6% of monosodium glutamate wastewater and 1.0 $g.L^{-1}$ of tryptone, resulting in a production of 2032 $mg.L^{-1}$ of surfactin. This result shows the advantage of recombinant strains regarding to wild strains for the production of surfactin.

Panjiar et al. (2020) reported the *Serratia nematodiphila* capacity of producing 4.5 $g.L^{-1}$ of glycolipids from hemicellulosic hydrolysates of rice straw and, in a lower concentration, 3.1 $g.L^{-1}$ of glycolipids in enzymatic hydrolysates (cellulosic). The glycolipid reduced the ST to 26 $mN.m^{-1}$ and exhibited emulsifying properties, since it emulsified 72%, 70%, 20% and 79.6% of hexane, xylene, diesel and palm oil, respectively. In addition to it, the glycolipid produced by *S. nematidophila* showed antimicrobial activity, in concentrations of 6.5 $\mu g.mL^{-1}$, 6.0 $\mu g.mL^{-1}$ and 10 $\mu g.mL^{-1}$, which inhibited the growth of *B. pumilus* (Gram positive), *P. aeruginosa* (Gram negative) and the yeast *C. tropicalis*, respectively.

Some studies demonstrate the production of biosurfactants by yeast in a synthetic medium using xylose as a carbon source. Faria et al. (2014) reported that yeasts *Pseudozyma antarctica* PYCC5048^T, *P. aphidis* PYCC 5535^T e *P. rugulosa* PYCC 5537^T, in a synthetic medium composed of xylose (40 $g.L^{-1}$), produce MEL in the concentration of 4.8, 1.2 and 2.8 $g.L^{-1}$, respectively. However, the maximum MEL productivity is 0.016 g / L / h obtained with the *P. antarctica* PYCC5048^T.

Joshi-Navare et al. (2014) reported that, when they cultivated *Pichia caribbica* in a synthetic medium containing 100 $g.L^{-1}$ of xylose, they obtained a xylolipid capable of reducing ST to 35.9 $mN.m^{-1}$ with a CMC of 1.0 $mg.L^{-1}$. In addition, the minimum inhibitory concentration of 0.025 $mg.mL^{-1}$ of the raw xylolipid inhibited the growth of Gram positive bacterium *Staphylococcus aureus*; this inhibitory action indicates that this biosurfactant can be used in medicines formulation.

Jain et al. (2013) also reported that *Klebsiella* sp. RJ-03 produces 3.0 $g.L^{-1}$ of biosurfactant in culture medium supplemented with 30 $g.L^{-1}$ of conventional xylose. The biosurfactant exhibited the ability of reducing ST to 48.17 $mN.m^{-1}$ and emulsifying compounds such as hexane, benzene, toluene, dichloromethane, carbon tetrachloride (50%), cotton oil and peanut oil (60%).

It is notable that those bacteria and yeasts produce biosurfactants either in synthetic medium containing commercial xylose or in medium containing hemicellulosic hydrolysates rich in xylose from different diluted acid-treated lignocellulosic biomasses. However, most studies reported in the literature use diluted acid as a pretreatment for lignocellulose, aiming to degrade hemicellulosic fibers leaving cellulose fibers exposed to enzymatic degradation, and consequent release of glucose monosaccharides, which are easily metabolized by microorganisms during fermentation processes. Another factor is that the concentration of by-products of enzymatic degradation is very low and does not influence the metabolism of microorganisms, unlike by-products generated from acid degradation.

It was also evident that, depending on the species when supplementing the medium with oily substrate, the output in the production of biosurfactants may increase. In addition, it may be necessary to supplement the hydrolysates with organic or inorganic nitrogen, as nitrogen is essential for the microorganisms' metabolism. Biosurfactants produced from hydrolysates have surface activity and emulsifiers and can be used in bioremediation of soils contaminated with hydrocarbons and, due to the insecticidal and antimicrobial action, they can be applied in the formulation of insecticides or medications.

6. Final Considerations

Furthermore, conventional sugar-based substrates can be replaced by lignocellulosic biomasses, whose hemicellulosic fibers are degraded and release fermentable sugars, when subjected to acid treatments, and those can be used in the production

of biosurfactants. This, in addition to reducing costs in the production of biosurfactants, also values waste and by-products of agro-industries, making it a sustainable alternative. It is also possible to note that, when using glucose as a carbon source, inhibition secondary metabolites production can occur, when compared to majority amounts of xylose.

With regard to microorganisms, the diversity in this group is famous, with biosurfactants types varying by genus. *B. subtilis* exhibited capacity to surfactin synthesis from hemicellulosic hydrolysates and in synthetic media supplemented with xylose. Yeasts can mainly synthesize glycolipids and lipopeptides with carbon sources from hemicellulosic hydrolysate, MELs and xylolipids, in synthetic medium. Thus, with the hemicellulosic hydrolysate rich in pentoses such as xylose, it is a possibility to increase the production of secondary metabolism products.

In summary, biosurfactants are multifunctional biomolecules because they exhibit different physicochemical properties, enabling them to be employed in different areas. Moreover, due to high biodegradability and low toxicity they are suitable to replace synthetic surfactants. The production of biosurfactants from hemicellulosic hydrolysates is promising, however, there is need for further investigations, because few microorganisms have the ability to metabolize xylose, present in hydrolysates, and produce metabolites with surfactant capacity. In the future, due to advances in genetic engineering, it is expected the production of strains (bacteria or yeast) with the ability to efficiently metabolize the different monosaccharides present in hydrolysates, thus having greater use of lignocellulosic biomass and also contributing to the management of agroindustrial waste.

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