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Review

Renewable, sustainable, and natural lignocellulosic carriers for lipase immobilization: A review

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ABSTRACT

It is well-known that enzymes are molecules particularly susceptible to pH and temperature variations. Immobilization techniques may overcome this weakness besides improving the reusability of the biocatalysts. Given the strong push toward a circular economy, the use of natural lignocellulosic wastes as supports for enzyme immobilization has been increasingly attractive in recent years. This fact is mainly due to their high availability, low costs, and the possibility of reducing the environmental impact that can occur when they are improperly stored. In addition, they have physical and chemical characteristics suitable for enzyme immobilization (large surface area, high rigidity, porosity, reactive functional groups, etc.). This review aims to guide readers and provide them with the tools necessary to select the most suitable methodology for lipase immobilization on lignocellulosic wastes. The importance and the characteristics of an increasingly interesting enzyme, such as lipase, and the advantages and disadvantages of the different immobilization methods will be discussed. The various kinds of lignocellulosic wastes and the processing required to make them suitable as carriers will be also reported.

1. Introduction

The use of biocatalysts such as enzymes has achieved a notable increase in the most varied industrial fields such as chemical, biochemical, pharmaceutical, medical, waste treatment, food and beverage, textile, pulp and paper, leather, biofuel, and animal feed (Mulinari et al., 2020). The interest is due not only to the possibility of improving the sustainability of a process (reduction of process time, low energy requirement, and non-toxicity) but also to the exceptional chemo-, regio- and enantio-selectivity of this kind of molecules. Furthermore, the development of recombinant DNA technology and bioengineering on unicellular life forms such as bacteria, fungi, and yeasts have given the possibility to further expand their applicability (Liu et al., 2013). As result, the total enzyme market was worth USD 9.9 billion in 2019 and the market for microbial lipases (triacylglycerol acyl hydrolases EC 3.1.1.3) is expected to grow by 7.1% in the next six years (Santos et al., 2021) reaching USD 590.2 million by 2023 (Chandra et al., 2020; Houde et al., 2004; Singh and Mukhopadhyay, 2012) thanks to their unique versatility and the fact that they can be easily and cheaply produced on large scale. Their role is to catalyze the hydrolysis of triglycerides into diglycerides, monoglycerides, and fatty acids but also a wide range of bioconversion reactions such as esterification, interesterification, aminolysis, and alcoholysis (Chandra et al., 2020; Rajendran et al., 2009). However, although the lipase-catalyzed processes have been extensively employed in different industrial fields (Chandra et al., 2020), their use is limited for the difficulty of recovery and reuse, long operational times, and low stability of the catalyst (F.L.C. Almeida, 2021). These drawbacks can be overcome by immobilization techniques which are becoming a flourishing developing field in chemical research.

While using supports may seem like an additional cost, it can lead to many overall economic benefits and savings. Indeed, the possibility to confine an enzyme on a solid matrix by physical or chemical interactions produces better stability against heat, pH, and denaturing agents, preventing the loss of the enzyme during the procedures. Moreover, it can also provide higher precision in the catalytic process control and allows the use of a multi-enzymatic system when needed. The main advantage, however, is that the recovery of the enzyme permits its recycling for various processes.

In the immobilization process, carriers and methods affect the biocatalyst properties and stability by causing a general increase in the protein's structural rigidity and resistance to different environmental factors (Mokhtar et al., 2020). Carriers should have a large surface area,

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high rigidity, and suitable particle size and must be resistant to microbial attacks. For lipase immobilization, various types of carriers are employed: inorganic materials of different sizes (micro, meso, and nano) (Costantini and Califano, 2021; Meena et al., 2021), DNA nanostructures (Thangaraj and Solomon, 2019a), metal-organic frameworks (MOFs) (Shomal et al., 2022), and, obviously, natural or synthetic polymers (Ismail and Baek, 2020; Thangaraj and Solomon, 2019a). DNA technology is based on the programmability of DNA hybridization for complex biomolecular nanostructures synthesis (Arora and Silva, 2018). Although it reduces the mass transfer resistance by controlling the relative positions and directions of enzymes in a confined space, this promising technology can hardly meet the requirements of large-scale industrial applications for the operation difficulty and high cost in the current stage. MOFs are formed from metal ions and ligands via coordination bonds in a porous crystalline structure. The high porosity and large surface-to-volume ratio indicate that MOFs could be ideal supports, but long-term water stability and the potential leaching of toxic metal ions still need to be addressed, especially considering the concept of green production (Xu et al., 2020). Finally, natural and synthetic polymers are the most common materials used in this field. From a comparison, it appears that even if the synthetic polymers show greater mechanical strength and versatility since they are selected according to the needs of the enzyme and the process, they require expensive and lengthy syntheses. Contrarily, natural polymers, although they may lack mechanical strength, still improve well catalytic performance, and may be directly used without any complex pretreatment (Zdarta et al., 2018). Furthermore, biopolymers possess unique characteristics, from biodegradability, harmless products, biocompatibility, and non-toxicity to an outstanding affinity to proteins (Alnoch et al., 2020). For instance, polysaccharides, cellulose, chitosan, alginate, and their derivatives, besides being renewable and easy to obtain, present reactive functional groups in their structure, mainly hydroxyl but also amine and carbonyl moieties, enable direct reaction between the enzyme and matrix (Bezerra et al., 2015). Therefore, the current industrial interest in clean, selective, and low-cost processes has drawn scientific attention to the research of new renewable supports for lipase immobilization. In this context, in the last decade, the focus has been placed on natural lignocellulosic materials discarded from the agro-industrial production chain thanks to their physical and chemical characteristics and to the possibility of transforming wastes into a source of new added-value compounds (Girelli et al., 2020; Melchor-martínez et al., 2022). In this way, lignocellulosic biomass can promote sustainability and alleviate existing pollution by reducing the rate of waste disposal. Generally, these by-product materials, generated in a million tons annually, are derived from the processing of agro-industrial products, such as rice, sugarcane bagasse, wood cellulignin, corn, coconut, spent grains, etc.

So, considering the topicality of the subject, the focus of this review is on the scientific attention in the 2000–2021 years for the lipase immobilization on lignocellulosic waste. The authors' prospect is to provide state-of-the-art perspectives for the support choice and experimental assessment. The review intends to guide readers and give them a useful tool to select the methodology that best suits them.

The review intends to guide readers and give them the knowledge required to broaden enzymes' application prospects in biotechnological processes that are still limited. It will present the various lignocellulosic wastes and the treatments required to use them as cheap and environmentally friendly supports. Furthermore, the immobilization conditions that are necessary to obtain an efficient solid biocatalyst from these carriers and an incredibly versatile enzyme (lipase) will be examined.

2. Lipases

According to "The lipase engineering database, " (2021) (LED), lipases are grouped into 38 superfamilies (6 for the class GGGX, 5 for the class Y, and 27 for the class GX) and 112 homologous families (22 in the first class, 8 in the second, and 82 in the last). Their molecular weights fall over a wide range (between 20 and 80 kDa) (Wijaya et al., 2020) and they are water-soluble like every enzyme. However, their peculiarity is that they can catalyze the hydrolysis of apolar substrates, generally water-insoluble, such as cholesteryl esters, triacylglycerides, wax esters, and di-monoacyl esters of glycerol (Brockman, 2013). They can perform these reactions thanks to their structure which allows a peculiar mechanism of action called "interfacial activation" that implies the adsorption of lipases on the hydrophobic surface of the substrate so that they can act at the apolar/aqueous interface (Brzozowski et al., 1991).

Most lipases, regardless of their origin or size, have a similar three-dimensional structure (α/β hydrolase fold) consisting of a central β-sheet formed by parallel filaments alternating with 4 α-helical segments (Pusch et al., 2022). In addition, the catalytic triad Ser-Asp/Glu-His is strongly conserved. The catalytic serine is situated in a very tight fold located at the C4 terminal end of the β5 filament, followed by an α-helix segment (Dasetty et al., 2017). This serine has an unfavorable conformation from an energetic point of view, called ε conformation, which allows the side chain of the serine to point toward the outside of the folding. The catalytic histidine, instead, is located at the C4 terminal end of the α/β folding last chain. The carboxylic acid residue can undergo some variations in position and nature, for example, aspartic acid can be found in *Rhizomucor miehei* lipase (Smith et al., 1992), while glutamic acid is the residue in *Geotrichum candidum* and *Candida rugosa* lipase (Cygler and Schrag, 1999; Smith et al., 1992). However, the C-terminal domain is always represented by a carboxylic functional group, while the N-terminal domain is a serine residue (Mukherjee, 2014).

The tertiary folding of the protein forms a three-dimensional network where hydrophobic groups are directed inwards and the hydrophilic groups protrude along the surface of the macromolecule giving stability to the enzyme and making it soluble in aqueous phases. In most lipase types is also present a mobile subdomain called "lid" that modifies its structure in the function of the environment (Khan et al., 2017). This lid assumes an "open" conformation in apolar solvents/substrates, while in polar solvents it can be "closed". In the first case, the lid permits the interaction with the substrate and the formation of products, while in the second situation, it covers the catalytic triad protecting it from the environment but also making it inaccessible to the substrates (Widmann et al., 2010). Fig. 1 shows the lid in an open conformational form and the catalytic triad of Ser-Asp-His structure of *Thermomices lanuginosus* lipase.

2.1. Lipases sources

Due to their key role in the metabolism of almost every species, lipases are ubiquitous. They are produced by a variety of organisms such

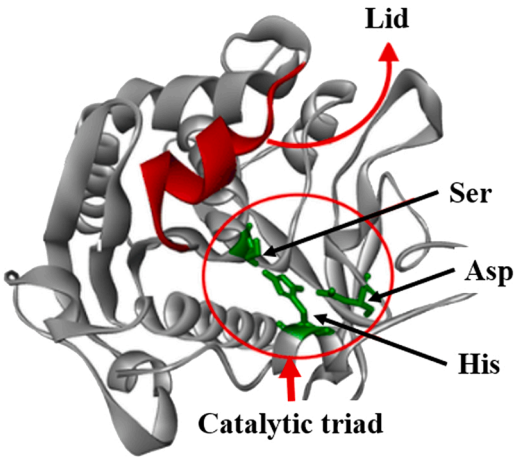

Fig. 1. *Thermomyces lanuginosus* lipase structure showing the lid and the catalytic triad (Ser-Asp-His).

as plants, animals, fungi, yeasts, and bacteria (Filho et al., 2019). The most widely used in biotechnological applications and organic chemistry are lipases of microbial origin (Chandra et al., 2020; Thakur, 2012). It is important to distinguish lipases from their sources because, as reported above, they belong to a large family. Depending on the organism that produces it, every lipase possesses different catalytic properties. Slight variation in the structure, correlated to the type of source, may lead to distinct conformations of the binding site and consequentially to various specific substrates for each kind of lipase (Widmann et al., 2010).

In plants, lipases represent an essential tool during their first development. They can be found, as well as in fruits, leaves, and grains, especially in the seeds. The seeds have a high oil concentration and, the necessity to break down these oils to obtain the energy needed for the sprout of the plant, leads to a high concentration of lipases too. For the same cause, the hydrolytic activity of the lipases in the seeds is much higher than the ones of other founds in different sections of the plant. Production of lipases from plants not only represents a means to recycle agro-industrial waste but is also an inexpensive process (Sarmah et al., 2018).

In animals, lipases are produced in two different ways: by specific cells belonging directly to the animal or by microorganisms present in their gastrointestinal tract. The most used lipase of animal origin is the porcine pancreatic lipase (Arumugam et al., 2018; Gong et al., 2013; Zhu et al., 2013), which is produced by genetically modified bacteria (Borrelli and Trono, 2015). In any case, animal lipases are rather difficult to extract, unless they can be produced from a modified microorganism, so they are not largely used for commercial purposes (Chandra et al., 2020; Yao et al., 2021).

Lastly, microbial lipases are by far the most studied and used, both for industrial and research purposes. They are mostly extracellular enzymes and are obtained from different kinds of microorganisms such as fungi, yeast, and bacteria, which lead to the possibility of having lipases characterized by great diversity and specificity (Verma et al., 2021). Furthermore, they have the advantages of being more abundant, cheaper, and easier to produce and genetically modify to obtain specific characteristics compared to the ones discussed above (Chandra et al., 2020). The lipases derived from the genus *Candida*, particularly from the species *Candida rugosa* and *Candida antarctica* (also known by the updated name *Pseudozyma antarctica*) ("UniProt - Enzyme database, ", 2021), are certainly the most exploited. Other largely used microorganisms are *Thermomyces lanuginosus*, *Rhizomucor miehei*, *Geotrichum candidum*, *Rhizopus oryzae*, *Cercospora kikuchii*, *Yarrowia lipolytica*, *Pseudomonas fluorescens*, *Acinetobacter baylyi*, *Burkholderia cepacia*, and *Chromobacterium viscosum* (Sandoval et al., 2017; Zago et al., 2021).

2.2. Lipase-catalyzed reactions

Lipases are enzymes that show high hydrolytic activity toward triglycerides, their natural substrates, from which they produce free fatty acids and glycerol (Rogalska et al., 1990). The hydrolytic reaction forms alcohol as the first product by nucleophilic attack of the active site serine on the carbonyl carbon of the ester bond (Fig. 2). The acyl-enzyme intermediate formed is subsequently hydrolyzed by water, forming carboxylic acid as the final product. In addition, other nucleophiles (e.g., hydroxylic compounds) can also deacylate acyl-enzyme intermediates leading to esterification and transesterification reactions. To make the esterification reaction thermodynamically favored instead of hydrolysis, organic solvents as reaction medium are introduced: initially water-miscible solvents (ethanol, acetone), then water-immiscible solvents, and, in recent papers, anhydrous organic solvents (Kumar et al., 2016). However, it is always preferable to keep a monolayer of water surrounding the enzyme when using an organic solvent since water preserves protein structure and the catalytically active conformation. So, the water content is one of the main factors in lipase-catalyzed esterification reactions since enough water must be present to retain the enzyme's active structure, and an excess value shifts the thermodynamic equilibrium toward hydrolysis over synthesis. For instance, Watanabe et al. (2001), showed that the equilibrium conversion for the CALB-catalyzed condensation of mannose and lauric acid in four different organic solvents (acetonitrile, acetone, 2-methyl-2-propanol, 2-methyl-2-butanol) is higher at lower initial water content and similar results were obtained in the fructose palmitate synthesis in 2-methyl-2-butanol (Chamouleau et al., 2001). So, in every lipase-catalyzed reaction, an optimal water amount must be employed, and its value depends on several factors such as the enzyme structure, reaction medium, and type of reaction. For example, Tsitsimpikou et al. (1997) reported two different optimal values of water activity (a_w) in the esterification reactions conducted with lipases from *Candida rugosa* and *Candida antarctica* in hexane (0.53 and 0.75, respectively). Valivety et al. (1992) stated that also *Rhizopus niveus*, *Humicola sp.*, *Candida rugosa*, and *Pseudomonas cepacian* lipases had different a_w values (consequentially higher) in an esterification reaction carried out in hexane.

Furthermore, the possibility to use lipases in a non-aqueous medium also offers the possibility to improve thermal stability, minimize the chances of contamination, and enhance hydrophobic substrates, besides shifting the thermodynamics equilibrium in favor of synthesis and suppressing undesirable water-dependent side reactions. In this way, lipases can catalyze different reactions, e.g., biotransformation of oils and fats, and offer a very important tool to synthesize various industrial products. However, the lipases' sensitivity to organic solvents is extremely different in function of their nature and the kinds of employed solvents. Usually, they are more unstable in polar-water miscible solvents than in water-immiscible solvents since polar solvents generally

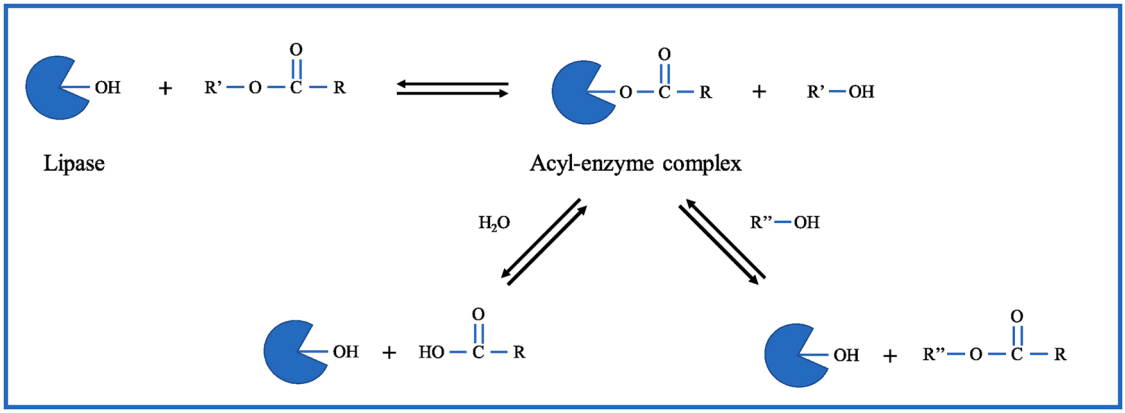

Fig. 2. Scheme of lipase-catalyzed esters hydrolysis (R′=alkyl group) and carboxylic acids esterification (R′=H) reactions.

tear off the tightly bound water from the enzyme hydration shells destabilizing the protein more than non-polar solvents (Banik et al., 2017; Bezsudnova et al., 2020; Kumar et al., 2016; Xue et al., 2022). It can be concluded that the enzymatic activity in organic media is primarily determined not by enzyme-solvent interactions, but by the water layer-enzyme interaction (Zaks and Klibanov, 1985). In the case of immobilized lipase, also the supports characteristics (particle size, surface area, porosity, and nature) play an important role because they affect water adsorption. The relative amount of water influences the proximity of the lipase active site to the water-organic interface and hence can impede substrate access. Therefore, the choice of solvent can influence the lipase reactivity, substrate specificity, regiospecificity, and enantioselectivity, and can promote the reaction conditions according to the specific requirements (Camacho Paez et al., 2003). Currently, the employment of lipases in organic solvents is in continuous increase and of immense interest in biotechnological uses such as biodiesel production. However, the volatility and toxicity of many conventional organic solvents are obvious drawbacks of this approach. To substitute the organic solvents, neoteric solvents such as ionic liquids (ILs) (Zhao et al., 2009), supercritical fluids (SCF), and deep eutectic solvents (DESs) have recently gained serious attention in biocatalysis since they are greener and environmentally benign (Dhake et al., 2013). Madeira Lau et al. (2000), stated that the lipase activity was increased in the presence of ILs as compared to organic solvents in the synthesis of non-enantio-selective esters using CALB. From a comparative study on the synthesis of isoamyl acetate in supercritical carbon dioxide (sc-CO_2) and conventional organic solvents using lipase, Romero et al. (2005) reported that the final esterification rate was similar in both media. Additionally, ester synthesis and transesterification reactions by free and immobilized lipase using DESs either as solvent, co-solvent, or even as combined solvent and substrate are reported (Pätzold et al., 2019). (Romero et al., 2005) (Madeira Lau et al., 2000).

However, lipases can catalyze other many reactions (Fig. 3), such as acidolysis for the synthesis of semi-solid fats by the incorporation of the desired acyl group onto a specific position of the triacylglycerol (Kavadia et al., 2018; Pacheco et al., 2010; Surendhiran et al., 2015; Xu et al., 2005), transesterification in the synthesis of fatty acid methyl ester (FAME) (Ryu et al., 2018; Xiaosan Wang et al., 2020), and they also can be useful in the separation of optical isomers from a racemic mixture in organic solvents, especially in the immobilized form (Bhardwaj and Gupta, 2017). Thus, lipases can be used in vitro to catalyze a great number of reactions aside from hydrolysis (its natural function), such as esterification, acidolysis, interesterification, transesterification, and aminolysis, together with a collection of the so-called promiscuous reactions (Ortiz et al., 2019). For these reasons, they are widely employed

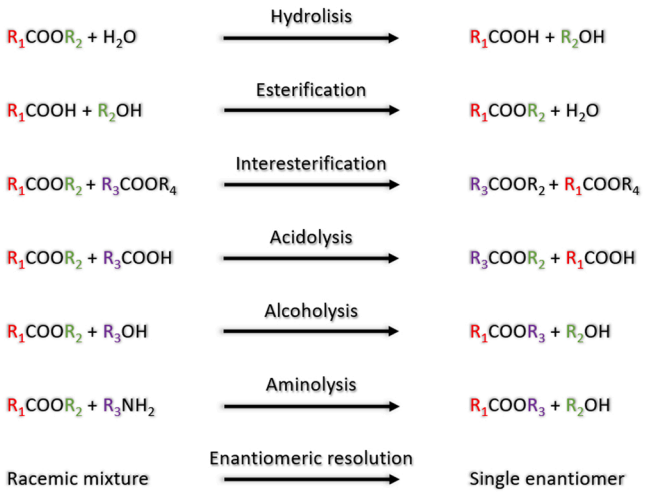

Fig. 3. Reactions catalyzed by lipases.

in the industrial field (Table 1). (Anderson et al., 1997; Ansorge-Schumacher and Thum, 2013; Aravindan et al., 2007; Bajaj et al., 2010; Gotor-Fernández et al., 2006; Hasan et al., 2010; Herrera-López, 2012; Jooyandeh et al., 2009; Nimkande and Bafana, 2022; Rodrigues and Fernandez-Lafuente, 2010; Tan et al., 2010).

3. Lipase immobilization on lignocellulosic waste

Immobilization is a powerful tool to improve enzyme characteristics (recovery, stability, selectivity, enantioselectivity, etc.) if the protocol is properly designed (Mateo et al., 2007). Several kinds of carriers have been studied over the years, especially synthetic polymers (e.g. acrylic, methacrylic, and styrenic resins) (Hanefeld et al., 2009), nanomaterials (Shuai et al., 2017) such as magnetic and inorganic nanoparticles (Liu et al., 2011) (e.g. nanogold (Du et al., 2013), graphene oxide (Kumar and Pal, 2021; Nematian et al., 2020) and silica nanoparticles), carbon-based and inorganic supports (silica and inorganic oxides of aluminum, titanium, and zirconium (Ismail and Baek, 2020)), and biopolymers (e.g. carbohydrates such as cellulose, starch, dextran, agarose and chitosan or proteins such as albumin and gelatin (Cantone et al., 2013)). Despite the advantageous characteristics of inorganic and synthetic materials, such as mechanical strength, nowadays researchers' efforts are focused on the development of more ecologically and economically favorable carriers which should preserve, or even improve, the stability and catalytic features of the enzymes (Thangaraj and Solomon, 2019a). In this context, the interest in lignocellulosic wastes as carriers for lipase immobilization is validated by the number of research paper publications in this area, and statistical data analysis evidence that the trend is constantly growing (Fig. 4).

Due to the constant rise in population, the world is experiencing an increase in forestry and agriculture activities. Thus, this economic sector produces billions of tons of vegetal waste biomass globally every year.

This kind of biomass is composed principally of wood and woody plants, grasses, and agricultural discard, so the main chemical components appear to be cellulose (16–50%), hemicellulose (10–38%), lignin (7–36%), and ash (0.4–15%), followed by a very low number of extracts (e.g., pectin, resins, waxes, etc.) and minerals. Cellulose is a linear polymer composed of about 10.000 glucose units linked by glycosidic bonds. It can form microfibrils with high crystalline structures thanks to cross-linked hydrogen bonds. The microfibrils are also associated to form macrofibrils or cellulosic fibers. These features affect the polymer properties, such as intra- and intermolecular bonds within the cellulose, and the structure can influence parameters such as solubility and chirality (Mokhena et al., 2021; Trache et al., 2020). Hemicellulose is an amorphous, low-weighted, highly branched heteropolysaccharide polymer. It is usually composed of 50–200 units of pentoses (e.g., D-xylose and L-arabinose) and hexoses (e.g., D-mannose, D-galactose, and D-glucose) and has the function of bonding together lignin and cellulose. In fact, unlike cellulose, it does not form microfibrils but can form hydrogen and covalent bonds between cellulose and lignin (Pasangulapati et al., 2012). Lignin is an insoluble heterogeneous, amorphous, and cross-linked aromatic polymer and is the cementing material that provides elasticity, hydrophobicity, and mechanical strength to the wood. Its main aromatic components are phenyl-propane units such as trans-coniferyl, trans-sinapyl, and trans-p-coumaryl alcohols. It is covalently linked to hemicellulose and represents the effective protective layer of biomass (Jeffries, 1994; Kumar et al., 2020). The general composition, as described right now, is shown in Fig. 5.

For lignocellulosic waste materials (e.g., spent grain, corn husk, sugarcane bagasse, etc.), the percentual chemical composition in cellulose, hemicellulose, and lignin is strongly influenced by the type of source and also by the age, climate, soil conditions as well as geographic locations of the plants (Harmsen et al., 2010). For example, coconut husk has the highest content of lignin (46.5%) whereas the loofah sponge has the greatest amount of cellulose (63%). Table 2 reports the percentual content of lignin, cellulose, hemicellulose, and ash in the

Table 1
Lipase-catalyzed reactions employed in the main industrial fields.

Field	Branch	Reactions	Products	References
Food	Diary	Hydrolysis of milk fat	Flavoring agent for diary industry	(Jooyandeh et al., 2009)
	Flavor	Esterification of short-chain fatty acids	Flavors for food industry	(Aravindan et al., 2007)
	Fats and oils	Hydrolysis, acidolysis, esterification of oils and fats	Fatty acids Diglycerides, monoglycerides Lipides of higher value with lower calories	(Rodrigues and Fernandez-Lafuente, 2010)
Medical	Diagnostics	-	Diagnostic kits for blood triglyceride assay	(Filho et al., 2019; Herrera-López, 2012)
Chemical	Chemical synthesis	Esterification Transesterification Hydrolysis Isomer resolution Isomer synthesis	Organi Synthetic molecules	(Anderson et al., 1997)
	Pharmaceutical	Esterification Acylation of bioactive molecules Isomer resolution Amine resolution Regioselective transformation	Drugs Single-isomer drugs	(Gotor-Fernández et al., 2006)
	Detergents	Hydrolytic removal of oil, stains, spots, and lipids	Detergent for laundry and household uses	(Hasan et al., 2010)
Environmental	Biofuels	Transesterification of triacylglycerol Esterification of free fatty acids	Biodiesel	(Bajaj et al., 2010; Tan et al., 2010)
	Bioremediation	Hydrolysis and transesterification of wastewater contaminants such as olive mill water and cooking oil waste	Less toxic compounds	(Nimkande and Bafana, 2022)
Cosmetics	Cosmetics	Hydrolysis, esterification acetylation	Cosmetic ingredients	(Ansorge-Schumacher and Thum, 2013)
Others	Paper, Textile, Leather	Hydrolysis	Removal of hydrophobic substances	(Houde et al., 2004)

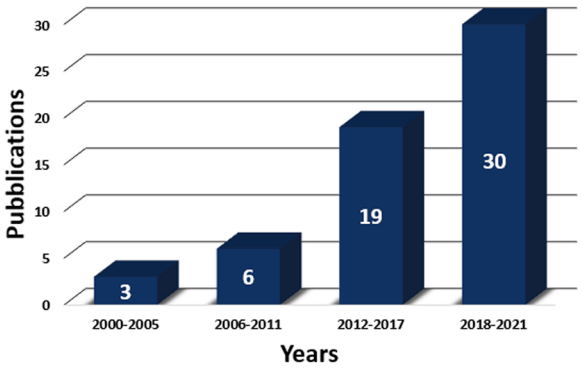

Fig. 4. Histogram of articles concerning lipase immobilization on lignocellulosic waste in the function of publication year (58 papers in total) from 2000 to 2021. Every bar corresponds to the number of papers published every 6 years, except for the last one which corresponds to 4 years. Data for 2021 may be incomplete since this survey was completed in November 2021.

main lignocellulosic wastes employed as carriers for lipases. Ash content reflects the amount of organic and inorganic matter available in the material and is normally present in low amounts (<5%) except for rice husk (15%). Generally, as reported by Alfaro et al. (2009) and Jústiz-Smith et al. (2008), the higher the ash percentage, the lower the carbon content. (Bilba et al., 2007; Cebreiros et al., 2018; Correia et al., 2013; da Costa Nogueira et al., 2018; de Carvalho Mendes et al., 2015; Hanum et al., 2017; Hu et al., 2014; Ikram et al., 2017; Lim et al., 2001; Nasution et al., 2020; Pippo and Luengo, 2013; Tanobe et al., 2005; Wahab et al., 2021; Xu et al., 2017).

To sum up, lignocellulosic waste is a very cheap and renewable feedstock, and it fulfills specific characteristics needed to be good enzyme support such as physical strength, inertness, and stability thanks to its composition (Rodríguez-Restrepo and Orrego, 2020). Anyway, it is decisive to implement the proper immobilization technique to profit from the best characteristics of every kind of waste.

3.1. Pretreatment of lignocellulosic material

Very often lignocellulosic carriers need to be subjected to pretreatments before being utilized in lipase immobilization. In this paragraph are discussed only those treatments which are independent of the immobilization reaction. However, all these pretreatments aim to improve the biocatalyst performance and to obtain the best experimental results in the function of waste type and immobilization method.

3.1.1. Washing and size control

Generally, the first steps are waste cleaning and drying. Since the cleaning solvent can affect the immobilized biocatalyst activity, it must be chosen very carefully in the function of the lignocellulosic waste selected. For instance, Palma et al. (2021) reported that the physical immobilization of *Rhizomucor miehei* lipase on bamboo powder washed with hexane gave better results than when the carrier was cleaned with sodium dodecyl sulfate or water.

The successive steps are generally the grinding and the sieving of the waste to obtain a homogeneous material of prefixed size except for green coconut fibers that are often used directly (Brígida et al., 2008). The support material particle size is also a decisive parameter to ensure the best biocatalyst performances. Yuan et al. (2021), comparing *Pseudomonas fluorescens* lipase immobilized onto rice straw filaments with the same lipase immobilized onto rice straw powder, evidenced different enzyme loading capacities (310 mg enzyme/g carrier and 380 mg enzyme/g carrier) and diverse activity attenuation after six reuses (8 h for cycle) in the transesterification of citronellol and vinyl acetate reaction system (0.36% h^{-1} and 0.32% h^{-1}).

3.1.2. Acid and alkali treatments

The low pH of the support material can be a limiting factor in the adsorption mechanism (as in the case of cellulignin (Gomes et al., 2005; Perez et al., 2007)) since the maximum adsorption is observed for pHs close to the isoelectric point of the lipases (pH 7–8) (Demirbaş et al., 2019). Therefore, when working with acid wastes, the neutralization with 0.1 M NaOH is a crucial process that cannot be avoided before the

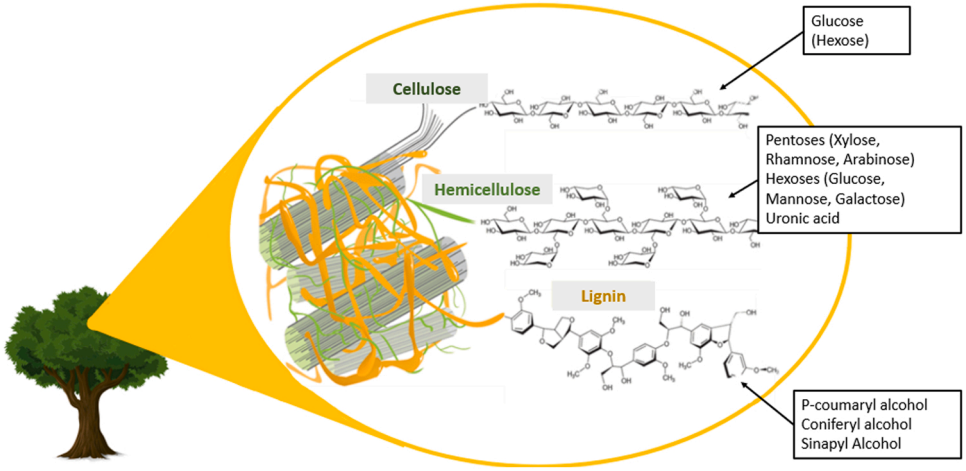

Fig. 5. Percentual composition of cellulose, hemicellulose, lignin, and ash of the main lignocellulosic waste material employed for lipase immobilization.

Table 2
Percentual content in lignin, cellulose, and hemicellulose in the main lignocellulosic wastes overviewed.

Waste	Lignin (%)	Cellulose (%)	Hemicellulose (%)	Ash (%)	References
Bamboo	27.80	37.50	27.90	1.20	(Hu et al., 2014)
Cashew apple bagasse	35.26	20.56	10.17	1.62	(Correia et al., 2013)
Coconut fiber	20.50	44.20	12.10	2.20	(Nasution et al., 2020)
Coconut husk	46.50	21.22	12.69	1.05	(Bilba et al., 2007)
Corn cob	18.40	30.00	34.00	1.60	(Xu et al., 2017)
Corn husk	7.90	35.30	37.50	5.00	(de Carvalho Mendes et al., 2015)
Corn stover	11.00	30.00	26.10	4.90	(Xu et al., 2017)
Green coconut fiber	35.70	32.80	15.90	3.60	(da Costa Nogueira et al., 2018)
Loofah sponge	11.20	63.00	19.40	0.40	(Tanobe et al., 2005)
Oil palm leaves	20.50	49.80	33.70	2.40	(Wahab et al., 2021)
Rice husk	21.44	32.24	21.34	15.05	(Hanum et al., 2017)
Rice straw	15.80	44.00	26.00	14.20	(Lim et al., 2001)
Spent grain	11.90–27.80	16.80–25.40	19.20–29.60	1.20–4.60	(Ikram et al., 2017)
Sugarcane bagasse	23.00	46.00	27.00	4.00	(Pippo and Luengo, 2013)
Wood cellulignin	28.40	44.20	13.50	0.50	(Cebreiros et al., 2018)

immobilization reaction.

Many times, chemical pre-treatments such as acid hydrolysis and alkali hydrolysis are also performed to make a partial or total delignification of the biomass to render cellulose more accessible, hence, facilitating the covalent binding of the lipase. Chemical treatment with acids (HCl or H_2SO_4) breaks the labile glycosidic bonds in hemicellulose causing its complete depolymerization by conversion of xylans into xylose and only a partial delignification of the material (Singh et al., 2014). In fact, the solubilization of hemicellulose promotes only a change in the lignin structure (Janker-Obermeier et al., 2012). Instead, the complete delignification is usually obtained by adding an alkali treatment (NaOH 0.5–1 M) at 120 °C after the acid treatment. This causes the saponification of the inter-molecular ester bonds between hemicellulose and lignin, permitting the complete removal of the latter and increasing the internal surface area of the material (Cui and Cai, 2018). The NaOH concentration can influence the immobilized lipase activity and the immobilization efficiency, but it is not possible to foresee the actual effects in every case because of the many variables involved in various immobilization procedures (type of carrier material, lipase, immobilization procedures – adsorption, covalent binding, entrapment, or cross-linking – and kind of other pretreatments applied, etc.). For example, Cui and Cai (2018) evidenced that NaOH hydrolysis did not affect the protein conformation utilizing bagasse as support, while Brígida et al. (2009) obtained a partial disintegration of the fiber and lower catalytic efficiency employing NaOCl for green coconut fiber.

3.1.3. Thermal treatments

Thermal treatments are also employed as lignocellulosic waste material pretreatments to obtain biochar, activated carbon, or ash. In the papers reviewed, biochar is obtained by guava seed or by *Manihot esculenta crantz* after pyrolysis at 500 °C (L.C. Almeida et al., 2021) or 600 °C (Oliveira-Ribeiro et al., 2019) under nitrogen stream, while activated carbon is obtained from corn husk after two steps of heating (550 °C for 2 h and 100 °C for 24 h) (Attan et al., 2019). Instead, ash is generally obtained by burning the material in the range 500–650 °C for 6 h in the function of the waste. In every case the materials thus formed are the pyrolysis product of the biomass and have very different characteristics from their precursors. They are principally formed by inorganic matter, especially carbon in activated carbon and biochar (Heidarinejad et al., 2020; Wang and Wang, 2019) and silica (amorphous silica and silicates) in ashes (Vassilev et al., 2013), and thus reflect the characteristics of their inorganic components. Silica is generally extracted from rice husk thanks to its high content in ash (15%) which is sharply above the average amount for lignocellulosic material (~ 4%). Bonet-Ragel et al. (2018a), comparing the performance of the biocatalyst obtained with rice husk ash (RHA) as support and the one synthesized with the commercial hydrophobic support OD403, showed how RHA could be considered a good alternative to commercial supports in biodiesel production.

3.1.4. Silica extraction

As above mentioned, the ashes obtained from the lignocellulosic waste biomass are rich in silica compounds, thus, some types like RHA and oil palm leaves ash (OPLA) are also used very often as renewable silica sources. To make this possible is necessary to follow a pretreatment process that includes a reaction with NaOH at high temperature to

form a sodium silicate solution, which is then treated with HCl to precipitate pure silica. This process presents the fundamental advantage of having a significantly lower environmental impact as compared to its commonly employed counterpart, i.e., sand (Handayani et al., 2022). Quartz extraction from natural sand exploits a non-renewable feedstock and not only destroys the natural landscape where the quarries are placed but also introduces a great number of pollutants into the environment both during the raw material acquisition and the lengthy procedures of silica extraction (Joglekar et al., 2019).

3.2. Immobilization reactions

The immobilization procedures can be divided into two main categories of methods: chemical and physical methods. Chemical methods imply strong covalent bonds between the enzyme and the support, whereas physical methods are based on weak interactions (affinity and ionic bonding, hydrogen bonds, hydrophobic interaction, van der Waals forces, and mechanical containment) (Mohamad et al., 2015). Following the research, it was pointed out how the most widely utilized method in lipase immobilization is physical adsorption, followed by covalent binding, entrapment, and cross-linking as shown in Fig. 6. The immobilization methods in relation to the type of waste supports, as well as the lipase sources, immobilization condition, and relative applications are reported in Table 3. (Abdulla et al., 2017; Arumugam and Ponnusami, 2013; Bonet-Ragel et al., 2018b; Brígida et al., 2007; Cespugli et al., 2018; Costa-Silva et al., 2013, 2021, 2018, 2016; Costa et al., 2014; Costa Silva et al., 2015; de Castro et al., 2001; de S. Lira et al., 2021; de Souza et al., 2020; De Souza et al., 2016; Deng et al., 2019; dos Santos Barbosa et al., 2020; Ferreira Nascimento et al., 2010; Gama et al., 2019; Ittrat et al., 2014; Jinda et al., 2003; Kaptan and Avcıbaşı-Güvenilir, 2018; Kumar and Kanwar, 2012; Lima et al., 2018; Lv et al., 2013; Machado et al., 2019a; Mendoza-Ortiz et al., 2020; Miguez et al., 2018; Mittersteiner et al., 2018; Nuraliyah et al., 2018; Onoja et al., 2018; Onoja and Abdul Wahab, 2019; Onoja and Wahab, 2020; Otari et al., 2020; Pospiskova and Safarik, 2012; Rizki et al., 2020; Rizki et al., 2020; Serpa et al., 2021; Spennato et al., 2021; Srisaipet et al., 2005; Ulker et al., 2016a, 2016b; Wong et al., 2019; Zainalabidin et al., 2014a, 2014b).

3.2.1. Adsorption

Adsorption is the simplest immobilization method and it relies on weak interactions such as London and Van der Waals forces, ionic bonds, hydrogen bonding, and hydrophobic interaction (Mohamad et al., 2015). Electrostatic and hydrophobic interactions are the most important (Mokhtar et al., 2020; Thangaraj and Solomon, 2019a) and are governed by several immobilization parameters: type of enzyme, surface area and chemical structure of the support, solvents and solutes present in the immobilization medium (Arana-Peña et al., 2020). Other determining factors are temperature, pH, quantity and quality of reagents,

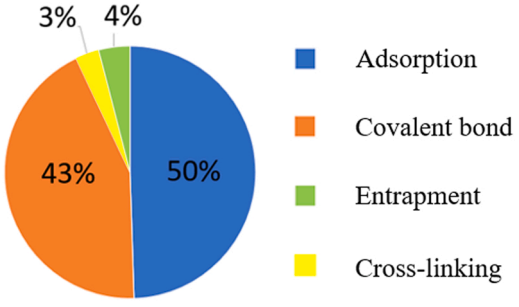

Fig. 6. Literature research related to lipase immobilization on lignocellulosic wastes (%) in the years from 2000 to November 2021. The percentage was obtained considering as total amount of every methodology utilized in the 58 papers reviewed.

ionic strength, and concentration of possible products (Zhang et al., 2013). Adsorption has several advantages that permit the exploitation of bioreactions in large-scale processes, such as mild and easy conditions, no need for additives, limited activation steps, the possibility to regenerate the support after use (Thangaraj and Solomon, 2019b), and inexpensiveness (Eş et al., 2015). Additionally, as only weak interactions are employed, no change in the native structure of the enzyme occurs, so there is a limited loss of enzyme activity during immobilization (Chakraborty et al., 2016). However, even if adsorption has many advantages, relying only on weak bonds usually results in low stability because the enzyme may easily desorb (Jesionowski et al., 2014).

Usually, lipase's physical immobilization on lignocellulosic waste is performed by simply mixing the enzyme with the properly pre-treated carrier under appropriate pH and ionic strength conditions for a certain incubation period. In this way, weak bindings, hydrogen bonding, and dipolar interactions between enzyme molecules and the waste surface can be established. Lignocellulosic waste materials such as rice (Abdulla et al., 2017; Bonet-Ragel et al., 2018a; Cespugli et al., 2018; de Castro et al., 2001; de S. Lira et al., 2021; Gama et al., 2019; Ittrat et al., 2014; Jinda et al., 2003; Kaptan and Avcıbaşı-Güvenilir, 2018; Lima et al., 2018; Machado et al., 2019a; Mendoza-Ortiz et al., 2020; Miguez et al., 2018; Santos et al., 2021; Ulker et al., 2016a; Yuan et al., 2021; Zainalabidin et al., 2014a, 2014b), sugarcane (Arumugam and Ponnusami, 2013; Mittersteiner et al., 2018), coconut (Brígida et al., 2009, 2008, 2007; de S. Lira et al., 2021; Ferreira Nascimento et al., 2010; Ittrat et al., 2014; Kumar and Kanwar, 2012), corn (Attan et al., 2019; Costa et al., 2014; Lv et al., 2013; Nuraliyah et al., 2018), bamboo (Arumugam et al., 2018; Deng et al., 2019; Palma et al., 2021), etc., are widely used in lipase adsorption because they present specific functional groups on their surface (hydroxyls, carboxyls, and phenyls) that can establish weak bonds with lipase. In addition, these waste materials have generally a high porosity - with different surface areas and pore sizes according to the material - which is a determining factor for the adsorption success (Alcañiz-Monge et al., 2022). In fact, it is well known that, in this case, the immobilization efficiency is highly influenced by the surface area and, especially, the pore size distribution of the carrier (Bayne et al., 2013). This implies that, as reported by Costa Silva et al. (2015) rice husk, coconut and corncobs having a higher specific area when compared with coffee grounds, sugarcane, and babassu mesocarp, and even microcrystalline cellulose present a higher immobilization efficiency. (Costa Silva et al., 2015; Wang and Wang, 2019). de S. Lira et al. (2021) described how the pores diameter and volume play a prominent role during the adsorption process as they affect the amount of enzyme that can be deposited within the pores themselves or the carrier surfaces. An ideal diameter range of 20–500 Å was found when *Thermomyces lanuginosus* lipase was employed. Moreover, the authors managed to increase the immobilized lipase activity by adding a degreasing pretreatment in a Soxhlet extractor with ethanol at 50 °C. This process led to the formation of new pores on the carrier that could act as new points of interaction.

As previously mentioned, other determining factors in the adsorption immobilization process are generally temperature, pH, protein loading, and ionic strength (Essa et al., 2007). In almost every paper concerning lipase immobilization on lignocellulosic wastes, the temperature is set at 25 °C (Table 3) since its effect on lipase immobilization is not relevant. Regarding the optimal value of loading protein, it is impossible to define a specific quantity since numerous waste materials, enzymatic sources, and methods of immobilization are used in the papers reviewed. It is however possible to establish the general rule that the adsorption efficiency increases with the concentration of protein during the loading step until the saturation of the support is reached. The ionic strength strongly influences the adsorption interaction and generally, a low value is preferred (de Lira et al., 2021). Indeed, in these conditions both hydrophobic and ion-exchange interactions improve. The hydrophobic interactions with the support are favored thanks to a decreased lipase solvation, whereas ion-exchanging gets better due to a minor

Table 3
Immobilization conditions, lipase source and applications, including the reactions and conditions, in function of support and immobilization method.

Support	Lipase source	Immobilization conditions	Application	Reaction	Experimental conditions	References
Immobilization by adsorption						
Babassu mesocarpus	*T. lanuginosus*	pH 7, 24 h, 25 °C	Hexyl laurate synthesis	Esterification	n-hexane, 1 h, 50 °C	(de S. Lira et al., 2021)
Bamboo	*C. antarctica*	pH 7, 24 h, 25 °C	Ethyl palmitate synthesis	Esterification	n-heptane, 50 °C	(Palma et al., 2021)
Bamboo	*C. antarctica*	pH 7, 24 h, 25 °C	(R)− 1-Phenylethyl acetate synthesis	Enantioselective esterification	cyclohexane, 48 h, 60 °C	(Palma et al., 2021)
Bamboo leaves ash silica	*Porcine pancreas*	pH 7, 24 h, 35 °C	Hydrolysis of rubber seed oil	Hydrolysis	water emulsion, pH 7, 30 °C, 8 h	(Arumugam et al., 2018)
Banana stalk	*A. baylyi*	pH 7.5, 6 h, 25 °C	Study of the enzyme-support system	Palm oil hydrolysis	-	(Ittrat et al., 2014)
Cashew apple bagasse	*C. antarctica*	pH 7, 24 h, 25 °C	Ethyl oleate synthesis	Esterification	solvent free, 24 h, 40 °C, 88.2%	(Serpa et al., 2021)
Cashew apple bagasse	*C. antarctica*	pH 7, 24 h, 25 °C	2-ethylhexyl oleate synthesis	Esterification	solvent free, 24 h, 40 °C,76.7%	(Serpa et al., 2021)
Cassava stump biochar	*Porcine pancreas*	pH 7, 24 h, 25 °C	Study of the enzyme-support system	Olive oil hydrolysis	pH 7, 37 °C, 30 min, 75% Arabic gum	(Oliveira-Ribeiro et al., 2019)
Coconut bark	*T. lanuginosus*	pH 7, 24 h, 25 °C	Hexyl laurate synthesis	Esterification	n-hexane, 50 °C, 1 h	(de S. Lira et al., 2021)
Coconut fiber	*C. antarctica*	pH 7, 2 h, 25 °C	Biodiesel production	Esterification	solvent free, 79% yield	(Ferreira Nascimento et al., 2010)
Coconut husk	*A. baylyi*	pH 7.5, 6 h, 25 °C	Study of the enzyme-support system	Palm oil hydrolysis	-	(Ittrat et al., 2014)
Coffee ground	*T. lanuginosus*	pH 7, 24 h, 25 °C	Hexyl laurate synthesis	Esterification	n-hexane, 50 °C, 1 h	(de S. Lira et al., 2021)
Corn cob	*T. lanuginosus*	pH 7, 24 h, 25 °C	Hexyl laurate synthesis	Esterification	n-hexane, 50 °C, 1 h	(de S. Lira et al., 2021)
Corn cob	*B. cepacia*	n-hexane, 2 h and then lipase l2h	Olive oil hydrolysis	Hydrolysis	pH 7, 55 °C	(Costa et al., 2014)
Corn cob	*A. baylyi*	pH 7.5, 6 h, 25 °C	Study of the enzyme-support system	Palm oil hydrolysis	-	(Ittrat et al., 2014)
Corn cob	*C. kikuchii*	PEG, 1 h, 25 °C	Study of the enzyme-support system	Olive oil hydrolysis	pH 6.5, 5 min, 40 °C, 3% Arabic gum	(Costa Silva et al., 2015)
Corn stover	*C. kikuchii*	PEG, 1 h, 25 °C	Study of the enzyme-support system	Olive oil hydrolysis	pH 6.5, 5 min, 40 °C, 3% Arabic gum	(Costa Silva et al., 2015)
Green coconut fiber	*C. antarctica*	pH 7, 2 h	Butyl butyrate synthesis	Esterification	n-heptane, 24 h	(Brígida et al., 2008)
Green coconut fiber	*C. antarctica*	pH 7	Study of the enzyme-support system	p-NPL hydrolysis	pH 7, 37 °C	(Brígida et al., 2009)
Green coconut husk	*C. kikuchii*	PEG, 1 h, 25 °C	Study of the enzyme-support system	Olive oil hydrolysis	pH 6.5, 5 min, 40 °C, 3% Arabic gum	(Costa Silva et al., 2015)
Guava seed biochar	*B. cepacia*	n-hexane, 15 min, then lipase pH 7, 3 h, 25 °C	Biodiesel production	Transesterification	solvent free, 40 °C	(L. C.F. xxxxxxx F.L.C. Almeida, F. L.C. Almeida et al., 2021, 2021; xxxxxxx L.C. Almeida, L.C. Almeida et al., 2021, 2021)
Palm fiber	*B. cepacia*	n-hexane, 15 min, then lipase pH 7, 3 h	Biodiesel production	Transesterification	96 h. 40 °C	(dos Santos Barbosa et al., 2020)
Corn stalk core	*P. aeruginosa*	pH 7, 1 h, 25 °C	Study of the enzyme-support system	Oil hydrolysis	pH 7, 1 h, 30 °C	(Lv et al., 2013)
Rice hull ash	*C. rugosa*	-	Enantiomeric resolution of R/S-α-Hydroxy Fatty Acids	Enantioselective hydrolysis	Tert-butanol	(Srisaipet et al., 2005)
Rice hulls	*A. baylyi*	pH 7.5, 6 h, 25 °C	Study of the enzyme-support system	Palm oil hydrolysis	-	(Ittrat et al., 2014)
Rice husk	*C. kikuchii*	PEG, 1 h, 25 °C	Study of the enzyme-support system	Olive oil hydrolysis	pH 6.5, 5 min, 40 °C, 3% Arabic gum	(Costa Silva et al., 2015)
Rice husk	*G. candidum*	Phenyl-silica activation, then lipase pH 7, 12 h, 25 °C	Decyl oleate synthesis	Esterification	n-heptane, 2 h, 50 °C	(Santos et al., 2021)
Rice husk	*T. lanuginosus*	n-hexane, 2 h and then lipase pH 7, 2 h, 4 °C	Hexyl laurate synthesis	Esterification	n-hexane 2 h, 37 °C	(de S. Lira et al., 2021)
Rice husk ash	*R. oryzae*	pH 7.5, 30 min, 4 °C	Biodiesel production	Transesterification	solvent free, 30 °C	(Bonet-Ragel et al., 2018b)
Rice husk ash	*C. antarctica*	pH 7, 5 h	Polycaprolactone synthesis	Esterification	toluene, 24 h, 60 °C, 77% yield	(Ulker et al., 2016b)
Rice husk ash silica	*C. viscosum*	pH 7, 4 h, 15 °C	Study of the enzyme-support system	p-NPP hydrolysis	30 min, pH 7, 37 °C	(Zainalabidin et al., 2014a)
Rice husk silica	*T. lanuginosus*	pH 7, 12 h, 25 °C	Cetyl oleate synthesis	Esterification	solvent free, 50 °C	(Gama et al., 2019)
Rice husk silica	*T. lanuginosus*	pH 4, 15 h, 25 °C	Decyl oleate synthesis	Esterification	solvent free, 180 min, 87% yield	(Miguez et al., 2018)
Rice husk silica	*T. lanuginosus*	OCTES (pH 5) or APTES (pH 4) activation, and then lipase 25 °C	Cetyl esters synthesis	Esterification	n-hexane, 94% yield	(Machado et al., 2019a)
Rice husk silica	*P. fluorescens* *C. rugosa* *T. lanuginosus*	OCTES activation, then lipase, pH 7, 25 °C, 18 h	Solketal palmitate synthesis	Esterification	n-heptane, 2.5 h, 56 °C, 83% yield	(Mendoza-Ortiz et al., 2020)

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Table 3 (*continued*)

Support	Lipase source	Immobilization conditions	Application	Reaction	Experimental conditions	References
Rice straw	*P. fluorescens*	water, 6 h, 37 °C	Citronellyl acetate synthesis	Transesterification	solvent free, 12 h, 37 °C, 99.8% yield	(Yuan et al., 2021)
Salacca wallichiana stem	*A. baylyi*	pH 7.5, 6 h, 25 °C	Study of the enzyme-support system	Palm oil hydrolysis	pH 8, 6 h, 60 °C	(Ittrat et al., 2014)
Spent grain	*C. rugosa*	pH 7.5, 20 h, 4 °C	Study of the enzyme-support system	p-NPB hydrolysis	pH 7.5	(Pospiskova and Safarik, 2012)
Sugarcane bagasse	*C. antarctica* *C. rugosa* *R. oryzae* *T. lanuginosus*	pH 7.2, 2 h, 35 °C	Enantiomeric resolution of (R,S)− 2-methylbutyric acid	Enantioselective esterification	n-hexane, 37 °C	(Mittersteiner et al., 2018)
Sugarcane bagasse	*C. kikuchii*	PEG, 1 h, 25 °C	Study of the enzyme-support system	Olive oil hydrolysis	pH 6.5, 5 min, 40 °C, 3% Arabic gum	(Costa Silva et al., 2015)
Sugarcane bagasse	*T. lanuginosus*	pH 7, 24 h, 25 °C	Hexyl laurate synthesis	Esterification	n-hexane, 1 h, 50 °C,	(de S. Lira et al., 2021)
Sugarcane leaf ash silica	*C. antarctica*	pH 7.5, 24 h, 37 °C	Biodiesel production	Transesterification	water (3% v:v), 8 h, 30 °C	(Arumugam and Ponnusami, 2013)
Sweet sorghum bagasse	*C. antarctica*	pH 7, 6 h, 25 °C	Methyl oleate synthesis	Esterification	solvent free, 12 h, > 92% yield	(Cui and Cai, 2018)
W. bifurcate leaves	*A. baylyi*	pH 7.5, 6 h, 25 °C	Palm oil hydrolysis	Hydrolysis	-	(Ittrat et al., 2014)
Wood cellulignin	*C. rugosa*	n-hexane, 1 h, then lipase, 2 h, 25 °C, PEG	butyl butyrate synthesis	Esterification	n-heptane, 37 °C, 48 h	(Gomes et al., 2005)
Immobilization by covalent bond						
Bamboo	*C. antarctica*	APTES and GLU activation and then lipase, pH 7, 24 h, 40 °C	Ethyl palmitate synthesis	Esterification	n-heptane, 50 °C	(Palma et al., 2021)
Bamboo	*C. antarctica*	APTES and GLU activation and then lipase pH 7, 24 h, 40 °C	(R)− 1-Phenylethyl acetate Synthesis	Enantioselective	cyclohexane, 48 h, 60 °C, pH 7, 24 h, 30 °C	(Palma et al., 2021)
Cashew apple bagasse	*C. antarctica*	GLU activation, pH 10	(R)-Indanol synthesis	Hydrolysis	-	(De Souza et al., 2016)
Cashew apple bagasse	*C. antarctica*	GEG activation, then lipase pH 7, 25 °C	Enantiomeric resolution of rac-indanyl acetate	Hydrolysis	pH 7, 24 h, 30 °C, 97% yield	(de Souza et al., 2020)
Cashew apple bagasse	*C. antarctica*	GLU activation pH 7, 24 h, 25 °C	Ethyl oleate synthesis	Esterification	solvent free, 24 h, 40 °C	(Serpa et al., 2021)
Cashew apple bagasse	*C. antarctica*	GLU activation and then lipase, pH 7, 24 h, 25 °C	2-ethylhexyl oleate synthesis	Esterification	solvent free, 24 h, 40 °C	(Serpa et al., 2021)
Corn cob	*C. kikuchii*	GLU or $NaIO_4$ or epichlorohydrine activation and then lipase PEG, pH 7, 25 °C	Butyl butyrate synthesis	Esterification	n-heptane, pH 6.5, 24 h, 35 °C	(Costa-Silva et al., 2021)
Corn cob	*C. kikuchii*	GLU activation, then lipase pH 6.5, PEG, 1 h, 25 °C	Study of the enzyme-support system	p-NPP hydrolysis	pH 6.5, 40 °C, 5 min, Triton X-100 0.4%, Arabic gum 0.1%	(Costa-Silva et al., 2013)
Corn husk leaf activated carbon	*C. rugosa*	pH 7, 25 °C, 24 h	Study of the enzyme-support system	Olive oil hydrolysis	pH 7, 37 °C, 30 min. Arabic gum 7%(w/v)	(Attan et al., 2019)
Corn stover	*C. kikuchii*	GLU or $NaIO_4$ or epichlorohydrine activation, PEG and then lipase pH 7, 25 °C	Butyl butyrate synthesis	Esterification	n-heptane, pH 6.5, 24 h, 35 °C	(Costa-Silva et al., 2021)
Corn stover	*C. kikuchii*	GLU activation, then lipase pH 6.5, PEG, 1 h, 25 °C	Study of the enzyme-support system	p-NPP hydrolysis	pH 6.5, 40 °C, 5 min, Triton X-100 0.4%, Arabic gum 0.1%	(Costa-Silva et al., 2013)
Green coconut fiber	*C. antarctica*	GPTMS activation, H2SO4 hydrolysis, $NaIO_4$ oxidation and then lipase pH 7	Butyl butyrate synthesis	Esterification	n-heptane, 24 h 0.30 °C	(Brígida et al., 2007)
Green coconut fiber	*C. rugosa*	GLU activation, PEG	Isoamyl caprylate synthesis	Esterification	isooctane, 40 °C, 48 h, 82.25% yield	(Costa-Silva et al., 2018)
Green coconut fiber	*C. kikuchii*	GLU or $NaIO_4$ or epichlorohydrine activation, PEG and then lipase pH 7, 25 °C	Butyl butyrate synthesis	Esterification	n-heptane, pH 6.5, 24 h, 35 °C	(Costa-Silva et al., 2021)
Green coconut fiber	*C. kikuchii*	GLU activation, then lipase pH 6.5, PEG, 1 h, 25 °C	Study of the enzyme-support system	p-NPP hydrolysis	pH 6.5, 40 °C, 5 min,	(Costa-Silva et al., 2013)

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Table 3 (*continued*)

Support	Lipase source	Immobilization conditions	Application	Reaction	Experimental conditions	References
Loofah sponge	*Porcine pancreas*	EDC/NHS activation and then lipase, pH 5.5, 4 h, 25 °C	Study of the enzyme-support system	p-NPP hydrolysis	pH 7.5, 37 °C, 0.4%	(Zhu et al., 2013)
Loofah sponge	*Porcine pancreas*	KIO4 oxidation and then lipase, pH 7.5, 1.5 h, 25 °C	Study of the enzyme-support system	p-NPP hydrolysis	pH 7.5, 37 °C, 0.4% TritonX-100, 0.1% Arabic gum	(Gong et al., 2013)
Oil palm leaves ash silica	*C. rugosa*	APTES and GLU activation, then lipase pH 7, toluene, 12 h, 25 °C	Butyl butyrate synthesis	Esterification	n-heptane, 45 °C, 3 h, 85.5% yield	(Onoja and Wahab, 2020)
Oil palm leaves ash silica	*C. rugosa*	APTES and GLU activation and then lipase pH 7, 20 min	Study of the enzyme-support system	Olive oil hydrolysis	pH 7, 30 min, 37 °C, Arabic gum (7%) (w/v)	(Wong et al., 2019)
Oil palm leaves silica	*C. rugosa*	APTES and GLU activation, toluene and then lipase pH 7, 12 h	Butyl butyrate synthesis	Esterification	n-heptane, 94% yield	(Onoja et al., 2018)
Oil palm leaves silica	*C. rugosa*	APTES and GLU activation, and then lipase pH 7, 12 h	Effect of Glu in butyl butyrate synthesis	Esterification	n-heptane	(Onoja and Abdul Wahab, 2019)
Rice husk	*B. cepacia*	GLU activation, then lipase for 20 min	Study of the enzyme-support system	Olive oil hydrolysis	Water, 37 °C, 30 min, Arabic gum 10%	(Abdulla et al., 2017)
Rice husk	*C. antarctica*	GLU activation and then lipase pH 7, 5 h, 25 °C	Polycaprolactone synthesis	Esterification	toluene	(Ulker et al., 2016a)
Rice husk	*C. antarctica*	$NaIO_4$ and HMDA activation and then lipase pH 8, 24 h, 25 °C	Dimethyl itaconate/ 1,4-butandiol polyester synthesis	Esterification	Solvent free, 50 °C, 70 mbar, 72 h	(Cespugli et al., 2018)
Rice husk	*C. antarctica*	$NaIO_4$ and HMDA activation and then lipase pH 8, 24 h, 25 °C	Propyl laurate synthesis	Esterification	solvent free, 55 °C	(Cespugli et al., 2018)
Rice husk	*C. rugosa*	GLU activation, PEG	Isoamyl caprylate synthesis	Esterification	isooctane,48 h, 40 °C, 88.71% yield	(Costa-Silva et al., 2018)
Rice husk	*C. kikuchii*	GLU or $NaIO_4$ or epichlorohydrine activation, PEG and then lipase pH 7, 25 °C	Butyl butyrate synthesis	Esterification	n-heptane, pH 6.5, 24 h, 35 °C	(Costa-Silva et al., 2021)
Rice husk	*C. kikuchii*	GLU activation and then lipase and PEG	Biodiesel production	Esterification	tert-butanol, 50 °C, 72 h	(Costa-Silva et al., 2016)
Rice husk	*C. kikuchii*	GLU activation, then lipase pH 6.5, PEG, 1 h, 25 °C	Study of the enzyme-support system	p-NPP hydrolysis	pH 6.5, 40 °C, 5 min, Triton X-100 0.4%, Arabic gum 0.1%	(Costa-Silva et al., 2016)
Rice husk	*T. lanuginosus*	GLU activation, then lipase pH 7, 48 h, 25 °C	Cetyl oleate synthesis	Esterification	n-hexane, 50 °C,9 h, 90.2% yield	(Lima et al., 2018)
Rice husk	*T. lanuginosus* *R. oryzae* *C. antarctica*	$NaIO_4$ or TEMPO/Laccase oxidation, then lipase, pH8, 24 h, 25 °C	Butyl butyrate synthesis	Esterification	isooctane, 45 °C, 21 h	(Spennato et al., 2021)
Rice husk ash	*C. antarctica*	GLU activation, and then lipase pH 7, 5 h, 25 °C	Polycaprolactone synthesis	Esterification	toluene, 30 °C, 72 h, 88.5% yield	(Kaptan and Avcıbaşı-Güvenilir, 2018; Ulker et al., 2016b)
Rice husk ash silica	*C. viscosum*	APTES activation and then lipase pH 7, 1 h, 15 °C	Study of the enzyme-support system	p-NPP hydrolysis	30 min, pH 7, 37 °C	(Zainalabidin et al., 2014a)
Rice husk ash silica	*C. viscosum*	APTES and carbodiimide activation, then lipase, pH7, 20 °C, 24 h	Study of the enzyme-support system	p-NPP hydrolysis	pH 7, 37 °C, 30 min, Triton X-100 0.4%, Arabic gum 0.1%	(Zainalabidin et al., 2014b)
Rice straw	*C. rugosa*	GLU activation, n-hexane, 2 h, then lipase in water and PEG, 2 h	Butyl butyrate synthesis	Esterification	37 °C, 24 h, > 70% yield	(de Castro et al., 2001)
Rice straw	*T. lanuginosus*	GLU activation and then lipase for 4 h, 4 °C	Biodiesel production	Esterification	water 10% (v:v), 45 °C	(Otari et al., 2020)
Spent grain	*C. rugosa*	GLU or $NaIO_4$ or epoxide or EDC/NHS activation and then lipase pH 7.5 20 h, 4 °C	Study of the enzyme-support system	p-NPB hydrolysis	pH 7.5	(Pospiskova and Safarik, 2012)
Sugarcane bagasse	*C. rugosa*	GLU activation, PEG	Isoamyl caprylate synthesis	Esterification	isooctane, 40 °C, 48 h, 83.87% yield	(Costa-Silva et al., 2018)
Sugarcane bagasse	*C. kikuchii*	GLU or $NaIO_4$ or epichlorohydrine activation, PEG and then lipase pH 7, 25 °C	Butyl butyrate synthesis	Esterification	n-heptane, pH 6.5,35 °C, 24 h	(Costa-Silva et al., 2021)
Sugarcane bagasse	*C. kikuchii*	GLU activation, then lipase pH 6.5, PEG, 1 h, 25 °C	Study of the enzyme-support system	p-NPP hydrolysis	pH 6.5, 40 °C, 5 min, Triton X-100 0.4%, Arabic gum 0.1%	(Costa-Silva et al., 2013)
Wood cellulignin	*C. rugosa*	GLU or CDI activation n-hexane, 1 h, then lipase, 2 h, 25 °C, PEG	Synthesis of butyl butyrate	Esterification	n-heptane, 37 °C, 48 h	(Gomes et al., 2005)

(*continued on next page*)

Table 3 (*continued*)

Support	Lipase source	Immobilization conditions	Application	Reaction	Experimental conditions	References
Wood cellulignin	*C. rugosa*	GLU activation PEG, n-hexane, 1 h, then lipase 2 h, 25 °C	Butyl butyrate synthesis	Esterification	solvent free, 24 h, 37 °C, > 88% yield	(Perez et al., 2007)
Immobilization by entrapment						
Rice husk ash silica gel	*Commercial lipase*	H_3PO_4 addition until pH 7	Palm oil hydrolysis	Hydrolysis	n-hexane, 2 h 25 °C	(Rizki et al., 2020)
Rice husk ash sol-gel	*P. sp. KLB1 lipase*	pH 7, 18 h, 25 °C, then n-hexane	Study of the enzyme-support system	Palm olein hydrolysis	water, pH 9, 60 °C, 1 h	(Jinda et al., 2003)
Coconut fiber	*Lipolase T20*	pH 8, 8 °C, overnight	2-octyl ferulate synthesis	Esterification	DMSO, 55 °C, 3 h	(Kumar and Kanwar, 2012)
Bamboo fiber	*C. sp. 99–125*	pH 7, 3 h, 30 °C	Wax esters synthesis	Transesterification	solvent free, 55 °C, 7 h	(Deng et al., 2019)
Immobilization by cross-linking						
Corn husk	*C. rugosa*	pH 7.5, 2 h, 25 °C and then 0.5% GLU	Olive oil hydrolysis	Hydrolysis	pH 7.5, 2 h, 25 °C	(Nuraliyah et al., 2018)
Spent grain	*C. rugosa*	pH 7.5, 20 h, 4 °C and then GLU 3 h, 4 °C	Study of the enzyme-support system	p-NPB hydrolysis	pH 7.5, 20 h, 4 °C	(Pospiskova and Safarik, 2012)

PEG = Polyethylene glycol; OCTES = Triethoxy(octyl)silane; APTES = (3-Aminopropyl)triethoxysilane; GLU = Glutaraldehyde; GEG = Glycidol-ethylenediamine-Glutaraldehyde; GPTMS = (3-Glycidyloxypropyl)trimethoxysilane; EDC/NHS = 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide/N-hydroxysuccinimide; TEMPO = (2,2,6,6-Tetramethylpiperidin-1-yl)oxydanyl; 960 CDI = Carbonyldiimidazole.

competition between media ions and protein ionic groups for the ionic sites the support. For example, Ittrat et al. (2014) reported that with a concentration of phosphate exceeding 20 mM the immobilized lipase activity on various agricultural wastes decreased.

However, the most influencing parameter is the pH as it is crucial both to maintain the active conformational form of the enzymes and to form interactions between the enzyme molecule and its carrier (Geluk et al., 1992),. Brígida et al. (2008) showed that pH affects immobilization yield and activity recovery of *Candida antarctica* lipase B (CALB) as it is related to the preservation of the conformational structure. Generally, when lipase adsorption on lignocellulosic waste is done directly or after acidic pretreatment, a neutral pH (pH 6–7.5) is usually employed (F.L.C. Almeida et al., 2021, L.C. Almeida et al., 2021, de S. Lira et al., 2021; Deng et al., 2019; dos Santos Barbosa et al., 2020; Ittrat et al., 2014), probably due to its proximity to the lipase isoelectric point. This feature is important in ionic-exchange interactions and not for hydrophobic ones, as reported in the literature (Gitlesen et al., 1997). In fact, when the lignocellulosic material is functionalized with triethoxy (phenyl)silane (Gama et al., 2019) or triethoxy(octyl)silane (Mendoza-Ortiz et al., 2020; Santos et al., 2021) to favor hydrophobic interactions with the enzyme the pH employed is usually 7 since any influence is not observed. Instead, on amino-functionalized rice husk silica (amino-SiO_2) *Thermomyces lanuginosus* lipase is strongly adsorbed in a pH range of 3–5 (Machado et al., 2019b). Considering the isoelectric points of amino-SiO_2 around 7 at alkaline values, the pH alters the balance between positive and negative charges on the support and enzyme surfaces and generates possible electrostatic repulsion between positive charges created on the two. When pH is low, the more protonated amine groups (NH_3^+) on the support surface cause an attraction increase with the negative charges on lipase with an isoelectric point at pH 4.4. Therefore, the optimal pH chosen was 4, a value also confirmed by Miguez et al. (2018).

In general, immobilization donates better thermal and operational stability to an enzyme (Basso and Serban, 2019; Lyu et al., 2021; Rodrigues et al., 2021). Usually, most immobilized lipases exhibit higher thermal stability than their free counterparts (Reshmi and Sugunan, 2013). This improvement is attributed to a minor sensitivity of the enzyme to thermal deactivation since its structure became more rigid after the immobilization (Guzik et al., 2014). Brígida et al. (2008) reported that CALB adsorbed on green coconut fiber had a significantly higher thermal stability than the soluble enzyme with a stabilization factor of 92.15. Costa et al. (2014) reported that the biocatalyst adsorbed on corn cob presented the same optimum temperature value at 50 °C but higher thermal stability (up to 80 °C) than the free enzyme. Zainalabidin et al. (2014a) demonstrated that the adsorbed lipase on mesoporous MCM-41 retained the activity better than free and even covalently immobilized lipase under various thermal stresses. However, in many cases the adsorption parameters must be optimized to obtain these results. In fact, Kaptan and Avcıbaşı-Güvenilir (2018) on the synthesis of polycaprolactone using CALB immobilized on rice husk ash activated with 3-aminopropyl) trimethoxysilane (APTES) reported that the lipase adsorbed on the waste had minor thermal stability compared to a commercial immobilized lipase (Novozyme 435) but in the optimal conditions (40 °C, 48 h), the authors reached an average molecular weight similar to the one obtained with Novozyme 435. It is worth mentioning that in the same paper has been reported that by adding a cross-linking factor (glutaraldehyde) the thermal stability of the waste-adsorbed lipase is equal to that of the commercial immobilized one.

High operational stability is another usual requirement when it comes to industrial applications since it allows the reuse of the enzyme in multiple cycles lowering the production costs (Hassan et al., 2019). Brígida et al. (2008) reported that, when lipase was adsorbed on green coconut fiber, the operational stability was higher in the organic synthesis of butyl butyrate than in the hydrolysis reactions of the same molecule. The authors hypothesized that the enzyme desorption during the reaction was favored when a hydrophobic substrate (methyl butyrate) was employed. However, it must be considered that in this case, the desorption had great influence because of the low enzyme loading obtained due to the nature of the coconut fibers which are scarcely porous and have low surface area. Generally, in studies on organic synthesis of esters like methyl oleate, cetyl oleate, and ethyl oleate, using oleic acid and the corresponding alcohols, the lipases adsorbed on lignocellulosic wastes always presented very satisfying results even after several consecutive reaction cycles: 12, 7, and 5, respectively (Cui and Cai, 2018; Gama et al., 2019; Serpa et al., 2021). Moreover, in the enantioselective esterification of (R,S)− 2-methyl butyric acid, even if the lipase adsorbed on sugarcane bagasse can only be reused for two cycles without a conversion rate decrease for the ester formation, it maintains the enantioselectivity for 4 cycles (Mittersteiner et al., 2018). Immobilized lipases are often used for enantioselective reactions, for example, *Candida rugosa* lipase immobilized on rice hull ash was employed for the resolution of (R/S)-hydroxy fatty acids in the presence of tert-butanol as a co-solvent for the substrate (Srisaipet et al., 2005).

When working with waste-adsorbed lipases the content of water role is also of vital importance because it may cause lipase aggregation and have negative effects on enzyme activity. Generally, in transesterification reactions water decreases the lipase reaction efficiency

(Costa Silva et al., 2015; dos Santos Barbosa et al., 2020). For example, dos Santos Barbosa et al. (2020) reported a decrease in the transesterification rate of crude coconut oil to ethyl esters from 72% in absence of any additives (water, tert-butanol, molecular sieve, and protic ionic liquids) to about 45% with water addition. To overcome this drawback Costa Silva et al. (2015) added a further dehydration step after the lipase immobilization on various lignocellulosic wastes before its application in the transesterification of olive oil. The authors evidenced that water presence can increase the rate of degradation reactions such as deamidation, oxidation, disulfide cross-linking, and Maillard reactions. In this context, the authors compared three different drying technologies: oven, freeze-drying, and spray drying concluding that the spray drier can be used for thermally sensitive materials as a higher lipase activity retention (in the range of 85.5% and 98.6% in the function of waste) was obtained. Yuan et al. (2021) synthesized cytronellyl-acetate even in a free solvent system confirming that also other solvents, like ether, acetone, n-hexane, etc., did not benefit the system. On the contrary, in hydrolytic reactions deionized water has to be used, being a reagent, as reported for coconut fiber (Brígida et al., 2008), sugarcane bagasse (Mittersteiner et al., 2018), cashew apple bagasse (De Souza et al., 2016), and other various agricultural byproducts (Costa Silva et al., 2015).

3.2.2. Covalent binding

The bibliographic research shows how the covalent binding between surface amino acids of the enzyme and the matrix is the second most used method for lipase immobilization. That is due to the formation of strong bindings that permit a minor enzyme leakage from the support during reactions and improve the system's reusability. Other advantages are the good control of the immobilized enzyme quantity and the evenness of the so-called self-assembled monolayer (SAM), a coating layer formed by the activation agent utilized during the preparation of the support (Nguyen and Kim, 2017). Furthermore, the great number of chemical reagents and protocols available for covalent enzyme immobilization makes this method very versatile (Alnoch et al., 2020; Zucca and Sanjust, 2014). As main disadvantages, there are the high risk of enzyme denaturation and the requirement for a high volume of bioreagent even if only a small amount of enzyme may be immobilized (~0.02 g/g of matrix (Nguyen and Kim, 2017)). Besides, even if the immobilization procedure largely increases enzyme stability, is poorly reproducible and it may decrease enzyme activity. In comparison to adsorption, covalent bonding requires a longer incubation time since the formation of SAM and the subsequent linkage of the enzymes to it takes several hours (Nguyen and Kim, 2017). The process is also more complex, and care must be taken to ensure the chemical purity required for a high SAM homogeneity. Generally, the active center amino acids in the enzyme are not involved in the covalent binding with the support but side chains of lysine (ε-amino group), cysteine (thiol group), and aspartic or glutamic acids (carboxylic group) are favored to achieve the highest enzyme activity level (Mohamad et al., 2015; Moreno et al., 1997).

The binding procedure of the enzyme to lignocellulosic solid support generally is carried out by initial derivatization of the support surface using condensing reagents, oxidative agents, or linker reagents (glutaraldehyde, epichlorohydrin, or carbonyldiimidazole), followed by the biocatalyst covalent coupling to the activated carrier, as shown in Table 3.

Zhu et al. (2013) reported a two-step process for lipase immobilization on loofah sponge waste. Activation of waste by citric acid addition to have free carboxylic acid and then lipase immobilization onto esterified loofah sponge by EDC/NHS mediated amine formation between carboxylic groups of the activated support with the amine groups of the enzyme. In particular, EDC reacts with the carboxylic groups on the loofah sponge surface forming an active O-acylisourea to react with NHS. Finally, the formed reactive esters can react with the enzyme amine group by covalent attachment of an acyl group to the nucleophile with the release of the NHS leaving group (Smith et al., 2020).

Oxidative agents can be KIO_4 (Costa-Silva et al., 2021; Gong et al., 2013; Perez et al., 2007) and laccase-TEMPO mediator systems (TEMPO-system) (Spennato et al., 2021). They are used to oxidize the cellulose component in lignocellulosic material with the difference that periodate causes the formation of two aldehydic groups by glucose cleavage (resulting in dialdehyde cellulose (Madivoli et al., 2019)), while the TEMPO-system forms a single carbonyl group which undergoes spontaneous oxidation to carboxylic groups. By comparison of the two methods, Spennato et al. (2021) reported that chemical oxidation was more efficient, but the biosystem provided a good non-toxic alternative.

Oxidation is also a useful process in the case a spacer needs to be inserted before the linker agent. Usually, the spacer is a diamine of various lengths as ethylenediamine (Attan et al., 2019) and hexamethylenediamine (Spennato et al., 2021; Cespugli et al., 2018;). The advantages of introducing a spacer are the minor steric interference of the support, more mobility of the enzyme groups involved in the immobilization, and more enzyme-support bonds (Rodrigues et al., 2021). Frequently glycidol is inserted on the surface of the carrier before the diamine and oxidized to form glyoxylic groups that react better with the spacer forming Schiff's bases (de Souza et al., 2020, 2016).

As concern the linkers, when compared with epichlorohydrin (Costa-Silva et al., 2021) and carbonyldiimidazole (Perez et al., 2007), glutaraldehyde (GLU) showed the best results in the activation of various agricultural by-products resulting in a higher lipase activity retention. The outcome was also better than the chemical oxidation with $NaIO_4$ of hydroxyl groups on supports.

In any case, GLU is the most utilized linker agent since it possesses two terminal carbonylic groups that can react to form imine binding preferentially with amino-terminal (pKa 7–8) and lysine ε-amino groups of the enzyme (pKa 10.7) on one side and, in the other side, with -OH and -NH_2 group of the support (Abdulla et al., 2017; Lima et al., 2018; Otari et al., 2020). Another reason of its popularity is the easy activation procedure that usually, is based simply in putting the pre-treated support in a GLU solution at controlled pH and room temperature for a congruous time. The support activation and the enzyme immobilization are highly influenced by GLU concentration and pH. By comparison of residual enzyme activities and operational stabilities of the *Cercospora kikuchii* lipase immobilized on various wastes (rice husk, sugarcane bagasse, green coconut fiber, corn stover, and corn cob) and microcrystalline cellulose, 1.5% of GLU resulted as the best concentration for each biocatalyst (Costa-Silva et al., 2013). As it may concern the pH, it affects not only the structure of glutaraldehyde since at acid and neutral pH it is a monomer and at alkaline pH is a polymer, but also the formation of Schiff's bases. In general, the preferred pH is 7, as reported by Costa-Silva et al. (2021) and Lima et al. (2018).

GLU is often used in conjunction with other agents such as spacer (diamines and glycidol), and oxidants as reported above, and with APTES and polyethylene glycol (stabilizer). APTES is used purely when working with silica or ash extracted from the lignocellulosic material of interest.

Silica possesses hydroxylic groups that can be silanized with APTES, leaving free ammine groups able to interact with GLU (Onoja et al., 2018; Onoja and Abdul Wahab, 2019; Ulker et al., 2016a; Wong et al., 2019). in a neutral medium (Pal et al., 2013), creating exceptionally stable covalent bonds with formation of Schiff's base.

It is also common to add polyethylene glycol (PEG) as a stabilizing agent when using glutaraldehyde as a linker (Costa-Silva et al., 2021, 2013; de Castro et al., 2001; Perez et al., 2007). This process can be due to the high physical adsorption of the PEG molecules to the hydrophobic area of the protein, which is generally associated with the lid and the surroundings of the active site, generating an improvement in the structural stability of the enzyme (Rawat et al., 2010; Rivero and Palomo, 2016). The increased lipase stability can lead to better results in catalytic processes; for instance, PEG improved *Candida rugosa* lipase

esterification activity in an organic medium when the enzyme was immobilized through GLU on grounded rice straw (de Castro et al., 2001). All the possible covalent immobilization strategies on lignocellulosic wastes are schematized in Fig. 8.

3.2.3. Entrapment or inclusion

Entrapment is a method based on enzyme dispersion within a solid or semi-solid matrix such as an organic polymer or a silica sol-gel. It represents a good strategy for preventing the denaturation of the fragile protein since no formal interaction is required, but this must be balanced against mass transfer limitations (Imam et al., 2021). Different methods of entrapment, such as temperature-induced gelation (e.g. agarose, gelatin), polymerization by a chemical/photochemical reaction (e.g. polyacrylamide), and ionotropic gelation of macromolecules with multivalent cations (e.g. alginate) can be used (Hassan et al., 2016).

Entrapment is a very versatile method since it can use various kinds of supports like gels of different natures, metal-organic frameworks (MOF) (Xiaoliang Wang et al., 2020), smart gels, 3D printing (Shao et al., 2022), hybrid materials, and ionic liquids (Imam et al., 2021).

The entrapment of enzymes in gels is generally a simple and practical method obtained via a mild process without affecting the enzyme structure (Deshmukh et al., 2020). The gels can be obtained with different textures: hard by sol-gel method, soft by the supramolecular assembly, and hard or soft in function of polymers and biopolymers used. Lipase immobilization on lignocellulosic waste exploits, generally, the sol-gel formation, as shown in Table 3.Jinda et al. (2003) and Rizki et al. (2020) chose silica from rice hush ash to form a rigid three-dimensional network of colloidal silica. The protocols implemented in the two papers contemplate the in-situ immobilization of lipase by a condensation process of the silica. In particular, the rice husk ash obtained from the rice husk incineration was previously extracted with NaOH. In this way, after filtration, the obtained alkaline yellowish solution, containing dissolved silica, was added to lipase and an acid solution until reaching pH 7 to form the gel with the entrapped lipase. Kumar et al. (2016) have synthesized 2-octyl ferulate in an organic medium employing an original network of coconut fibers with Lipolase T20 trapped within their pores. They exploited the use of a cross-linking agent (Glu) that reacted with the high amount of -OH in the fibers to form a complex lignocellulose structure.

Another original core-shell structure of lipase immobilized was reported by Deng et al. (2019) employing bamboo fibers as support. In this case, sodium alginate addition gathered the bamboo carrier into granules, so the adsorbed immobilized lipase turned into a porous status. The successive addition of calcium chloride made the granules coat a rigid film, which increased the stability by preventing the leakage of the enzyme molecules.

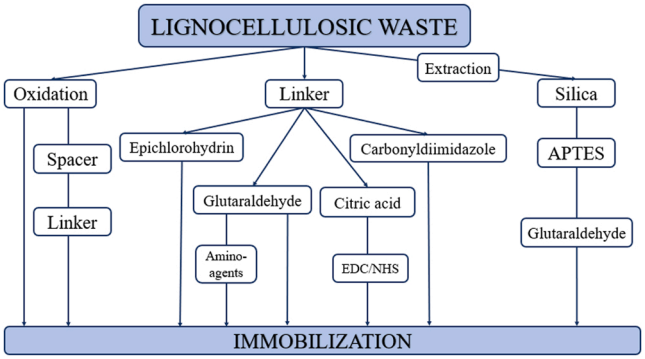

Fig. 8. Scheme of possible strategies of lignocellulosic waste pretreatment and activation for covalent lipase immobilization.

3.2.4. Cross-linking

The cross-linking can be partially categorized as covalent bonding, as the enzymes are covalently connected to each other by a cross-linking agent (usually glutaraldehyde) forming extended and complex three-dimensional structures. These many intramolecular bindings permit an increase in the biocatalyst's structural rigidity, improving its stability. This factor, together with the simplicity of execution, make cross-linking one of the most convenient immobilization methods. Nevertheless, its main disadvantage is the potential inactivation of the enzyme during the immobilization, which is a major drawback to its applicability. Indeed, creating all these bonds exponentially increases the probability of enzyme inactivation (Elnashar, 2011). Cross-linking can be used to form support-free structures known as cross-linked enzyme aggregates (CLEAs) (Yamaguchi et al., 2018). However, these aggregates have poor mechanical properties, so cross-linking is rarely used as the only means of immobilization. In the majority of cases, it is used in combination with adsorption following a two-step process: i) adsorption of the enzyme on the surface of a solid carrier and ii) cross-linking with glutaraldehyde. The adsorption can be performed directly on the carrier or after its activation with an anionic exchanger, e.g., polyethyleneimine (PEI).

Only two papers were found that discussed the immobilization of

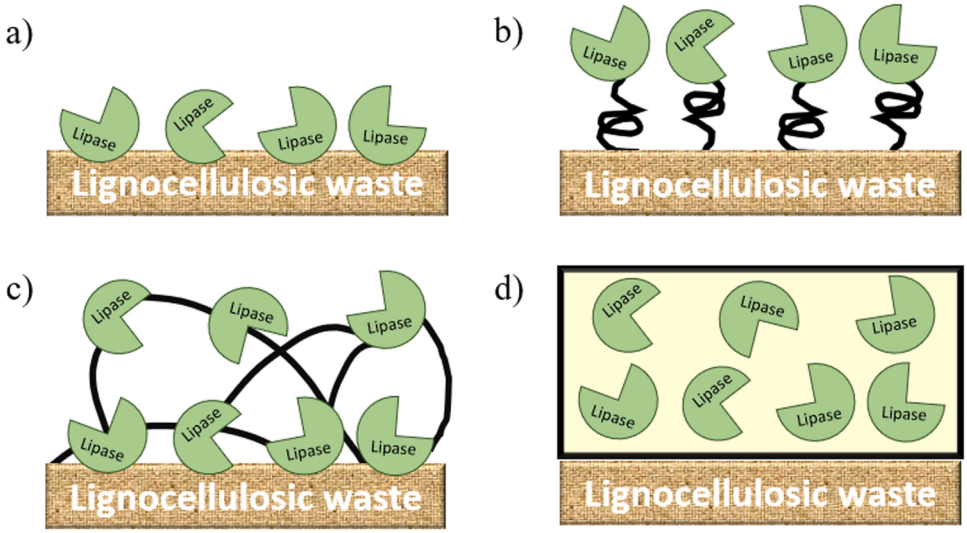

Fig. 7. Schematic representation of the different immobilization methods of lipase on lignocellulosic waste: adsorption (a), covalent binding (b), cross-linking (c), and entrapment (d).

lipase on lignocellulosic supports via cross-linking (Nuraliyah et al., 2018; Pospiskova and Safarik, 2012). Pospikova and Safarik (2012) synthesized a solid biocatalyst with *Candida rugosa* lipase cross-linked on magnetically modified spent grain. This work is particularly interesting because the authors compared the performance of the biocatalysts obtained by cross-linking (with and without PEI activation) with the ones obtained by adsorption and covalent methods. The research demonstrates how the biocatalyst obtained by cross-linking with PEI activation retained 100% of its activity after 30 days storage at 4 °C. Furthermore, it had better operational stability compared to all others and was reused 8 times in 4-nitrophenyl butyrate hydrolyzation without any activity loss. Nuraliyah et al. (2018) also demonstrated how cross-linking with 0.5% glutaraldehyde may improve the performance of a biocatalyst immobilized by adsorption in the optimal immobilization conditions (0.75 mg/mL of *Candida rugosa* lipase solution and 4 h of reaction time).

4. Applications

As shown in Table 3, the lipase immobilized on agro-industrial wastes has been applied successfully for different purposes, like the synthesis of compounds of scientific or industrial interest (butyl butyrate, hexyl laureate, decyl oleate, polycaprolactone, ethyl palmitate, citronellyl acetate, etc.) by esterification and enantiomeric resolution of rac-indanyl acetate and R/S-α- Hydroxy Fatty Acids by hydrolysis. However, the most innovative and "greener" application is biodiesel production, which is a great potential alternative to conventional fuels. This goal was pursued by many authors using lipase from different sources (*B. cepacea, C. antarctica, C. kikuchii, T. lanuginosus, R. oryzae*) immobilized on various lignocellulosic materials (coconut fiber, palm fiber, rice straw, rice husk, rice husk ash, sugarcane leaf ash). For this application, adsorption and covalent binding were used as immobilization methods and the biocatalysts synthesized were used in the transesterification reaction of natural oils to fatty acid methyl esters (FAME) and ethyl esters (FAEE) using methanol or ethanol as acyl acceptor, respectively. The reactions occurred at different temperatures, in a 30–45 °C range for FAME and between 40 and 50 °C for FAEE. Interesting results were obtained by Costa-Silva et al. (2016) which obtained a 98.1% FAEE conversion after 72 h at 50 °C with a final amount of mono- and diacylglycerols of 0.4% and 0.5%, respectively, in accordance with the ASTM standard for biodiesel (ASTM D6751). dos Santos Barbosa et al. (2020) in the transesterification of crude coconut oil with ethanol catalyzed by lipase immobilized on palm fiber reached 72% yield at 40 °C and after 96 h reaction. It is worth mentioning that the authors are the only ones who have studied the influence of ILs on the catalytic reaction, but they found a decrease in conversion to FAEE dependent on the concentration and alkyl chain length of ILs. Arumugam and Ponnusami (2013) reached a FAME yield of 98.6% in a very short time (8 h) and at a low temperature (30 °C) which decreased only by 8.9% after eight recycles. In this way, the main disadvantages in alkali or acid-catalyzed processes, such as high energy requirements, difficulties in the recovery of the catalyst and glycerol, and potential pollution to the environment, can be overcome with a reduction of the process cost (Rodrigues et al., 2017). Hence, the using of enzyme catalysis for the industrial production of biodiesel might soon have a bright future.

5. Advantages and disadvantages

It is very hard to compare the catalytic characteristics of biocatalysts obtained with different supports as each method has its optimal conditions (pH, time, temperature, medium, enzyme source, etc.), so researchers focus the comparison with commercial immobilized lipase. With this aim, the papers reporting the comparison made by the same author and the in same experimental conditions were considered. In Table 4, the advantages and disadvantages of lipase immobilized on some lignocellulosic waste carriers are summarized. It appears that these supports, in addition to being available and cheap, can be a valid alternative for the preparation of biocatalysts with further benefits. When compared with the most widely used commercial immobilized lipase in both academy and industry (Novozyme 435) (Ortiz et al., 2019) in esterification reactions, similar or higher conversions were obtained (Brígida et al., 2008; Kaptan and Avcıbaşı-Güvenilir, 2018; Mittersteiner et al., 2018; Ulker et al., 2016b; Yuan et al., 2021). Besides, de Lira et al. (2021) reported higher esterification activity of the biocatalysts obtained with babassu mesocarp and rice husk (141.4 e 396.4 U/g) and lower hydrolytic activity (5.331 e 4.608 U/g) when compared with the 113.5 U/g and 142 U/g activities, respectively, obtained with the commercial Lipozyme TL 1 M (*Thermomyces lanuginosus* lipase on granulated silica). Bonet-Ragel et al. (2018) demonstrated instead that the lipase immobilized on rice husk ash was a valid alternative to Relizyme OD403 (Mitsubishi Chemicals, 2021) in biodiesel production since similar reaction rate and yields (64%) after 26 h of reaction were obtained. Ferreira Nascimento et al. (2010), also achieved good results employing coconut fiber as the carrier for FAEE synthesis from macauba oil with a conversion of 79% in 72 h against 85% with Novozyme 435.

6. Conclusion and future perspectives

Lipase immobilization is a promising strategy for improving the efficiency and economics of various biotechnological and industrial applications as it reduces the overall operating cost of a chemical process,

Table 4
Advantages and disadvantages of lipase immobilized on lignocellulosic waste compared to common commercial immobilized lipases.

Lignocellulosic waste	Commercial immobilized lipase	Application	Advantages	Disadvantages	Reference
Rice husk ash	Novozyme 435	Polycaprolactone synthesis	Similar conversion (~90%)	Lower thermal stability	(Kaptan and Avcıbaşı-Güvenilir, 2018)
Rice husk ash	Novozyme 435	Polycaprolactone synthesis	Low PDI values, high molecular weight, and conversion (~84%)	-	(Ulker et al., 2016b)
Rice straw	Novozyme 435	Citronellyl acetate synthesis	Similar conversion (~90%) with lower energy consumption	-	(Yuan et al., 2021)
Coconut fiber	Novozyme 435	Butyl butyrate synthesis	Similar conversion (~90%)	Less operational stability	(Brígida et al., 2008)
Coconut fiber	Novozyme 435	Biodiesel production	Similar conversion (~80%)		(Ferreira Nascimento et al., 2010)
Bamboo powder	Novozyme 435	Kinetic resolution of rac-1-phenylethanol	Same enantiomeric excess with half protein loading	Lower conversion	(Palma et al., 2021)
Babassu mesocarp	Lipozyme TL 1 M	Hexyl laureate synthesis	Higher esterification activity	Lower hydrolytic activity	(de S. Lira et al., 2021)
Rice husk	Lipozyme TL 1 M	Hexyl laureate synthesis	Higher esterification activity	Lower hydrolytic activity	(de S. Lira et al., 2021)
Rice husk ash	Relizyme OD403	Biodiesel production	Same reaction rate	-	(Bonet-Ragel et al., 2018a)

lowering the energy required and improving the stability of enzymes.

Therefore, following the current industrial approach focused on environmental and economic sustainability, there is a considerable and rising demand for new immobilized biocatalysts, given their positive environmental impact. In the literature, several reviews on a new variety of organic and inorganic supports for lipase immobilization are reported, but without including the development of innovative waste utilization techniques. Their use is a promising alternative since they are highly available, cheap, easily functionalizable, mechanically stable, biodegradable, and stable in harsh environments. Therefore, this review is focused on the recent progress in the lipase immobilization methods on these renewable materials and the proposed applications. Even if it is impossible to summarize a unique methodology since each waste requires different pretreatment steps according to their composition, the results show that adsorption is the preferred method and generally is performed at pH 7 and 25 °C independently of the waste used. It is worth highlighting how coconut is the waste most used in the adsorption method, while rice scraps are in covalent immobilization. These features can be due to the high lignin content that favors hydrophobic adsorption in coconut, and a high level of silica in rice, which thanks to its -OH reactive groups, is a very idoneous material for covalent immobilization.

Furthermore, lignocellulosic wastes are biodegradable and non-toxic, can be used directly or with little modifications as lipase carriers, and have the potential to fulfill one of the gaps in agricultural waste management. In addition, the biocatalysts have high operational stability that makes them feasible for the synthesis of several products such as hexyl laurate, ethyl palmitate, butyl butyrate, polycaprolactone, etc.

It is relevant to mention that, in the last years, these immobilized biocatalysts were also used in biodiesel production, a promising field for environmental research. In particular, coconut fiber, guava seeds biochar, and rice husk ash have been successfully applied in solvent-free reactions, leading to an economical advantage, especially in large-scale industrial production. Although they are good alternatives to the commercial biocatalysts commonly used, further studies are needed to favor the commercial distribution of lipase in the industrial field. Accordingly, the hope is that many new lignocellulosic wastes with different properties (porosity, surface area, hydrophobicity, etc.) and immobilization procedures will be reported for lipase-catalyzed processes in the upcoming years, especially in the environmental field, as biofuel production.

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CRediT authorship contribution statement

Anna Maria Girelli: Conceptualization, Investigastion, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, **Viviana Chiappini**: Conceptualization, Investigastion, Writing – original draft, Writing – review & editing, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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