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REVIEW

Immobilization of enzymes and cells on lignocellulosic materials

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Abstract
The rising activities of global agriculture and forestry industries are producing huge amounts of lignocellulosic waste, which needs to be well recycled. The management of this waste involves environmental, social, economic and political challenges. Lignocellulosics have been commonly used for construction materials and energy production, thus achieving positive social and environmental impacts. Lignocellulosics represent also a promising feedstock for the production of carriers for enzyme and cell immobilization. Immobilization is a technique in which the biocatalyst is fixed on the surface of an insoluble matrix, allowing to recover the biocatalyst after reaction. The support must have specific characteristics such as inertness, physical strength, stability, renewability and low cost. These characteristics are fulfilled by lignocellulosic materials. Here, we review the applications of lignocellulosic biomass for fermentation, remediation of contaminated water and soil, synthesis of solvents and fine chemicals, juices clarification, and production of fructooligosaccharides. Recycling lignocellulosic waste for the immobilization of enzymes and cells allow to reduce environmental issues. Processes using immobilized cells and enzymes give high rates of solvent productivity, of 1.44–1.67 g/Lh, activity retention, around 90%, and stability, above five cycles of reaction.

Keywords Lignocellulosic wastes · Enzymes · Cells · Support for immobilization · Biocatalysis · Waste management

Introduction

Generally, biocatalytic processes can be simpler to operate than chemical processes; they are very competitive due to their environmental profiles. Processes such as heterogeneous catalysis, flow chemistry, continuous processing, green solvents, catalyst immobilization, and recycling are some of the main relevant and emerging technologies that hold great potential for clean and selective production processes (Gericke et al. 2015). Biocatalysis has been widely accepted in different economic sectors, owing to its substrate specificity and green chemistry characteristics by which transformation reactions are carried out under mild conditions of temperature, pressure and pH (Datta et al. 2012). Biocatalysis is an energetically efficient and sustainable technique that produces the lowest waste and can be used in a variety of scientific and industrial applications. However, the use of biocatalysis is restricted because of its long operational time, stability, difficult recovery and reuse of the catalyst. These issues can be overcome through the immobilization (Sheldon and Van Pelt 2013). Immobilization of cells and enzymes is a biotechnological technique in which these biocatalysts are fixed in a suitable matrix that limits their movement to increase their stability and reusability. Immobilization has been widely researched, and a lot of reviews focusing on techniques to immobilization of enzymes, and in the use of organic and inorganic carriers to immobilization have been published (Velasco-Lozano et al. 2016; Bilal and Iqbal 2019; Thangaraj and Solomon 2019). Even, works in immobilization of cells (Bouabidi et al. 2018) on organic waste as eggshell (Salleh et al. 2016), and recently trends in immobilization onto novel materials such as magnetic nanoparticles have been published (Mehta et al. 2016; Vaghari et al. 2016; Khoshnevisan et al. 2017). These studies have demonstrated that when the carrier fulfills with physical, chemical, electrical, or mechanical characteristics, the activity and stability

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of the biocatalysts can improve across a broader range of operating conditions (Chapman et al. 2018).

Spite the fact that the immobilization has several advantages as functionality for use in continuous processes and easy separation of the enzyme from the medium of reaction, and reuse of the enzyme. The cost of the carrier and its additional preparation materials and methods is a disadvantage that limits in some cases the use of carriers. So, it is important that the immobilized systems provide positive economic benefits that can overcome and balanced the additional costs associated with the materials used as carriers (Chapman et al. 2018).

One interesting option that contributes to reducing immobilization costs is the use of natural supports from lignocellulosic materials (Fig. 1) that are cheaper than other kind of supports and are widely available in the world. Lignocellulosic carriers also have desirable physical and mechanical properties, and they are environmentally friendly, renewable, biodegradable and nontoxic (Moniruzzaman and Goto 2016), which make their use and industrial scale implementation easier (Velasco-Lozano et al. 2016; Thangaraj and Solomon 2019). In fact, several authors have evaluated the use of lignocellulosic biomass as a carrier to immobilization. They have demonstrated the success of these systems in several biotechnological, pharmaceutical and environmental fields. However, there are no reviews that summarize these efforts and let the academic community to know about the exclusive use of lignocellulosic biomass as carrier for immobilization. For that, taking into account the above-mentioned considerations, this review makes a special emphasis on the use of lignocellulosic biomass to immobilization of enzyme and cells. Besides describing the most commonly used enzymes and cells and their uses, this review provides descriptions of raw materials, pretreatments and the methods used to activate the carrier according to the method of immobilization.

Lignocellulosic biomass

Globally, billions of metric tons of biomass are produced directly from agricultural activities including crop-based and agro-industrial residues and by-products. Tons of dry biomass (DM) has been used for feed (58%), bioenergy (heat and electricity, 16%), food (14%), materials (10%) and biofuels (1%) (Schröder et al. 2018). As improper management of large amounts of biomass causes environmental problems due to difficult disposal or reuse, enormous efforts are being made to explore innovative alternatives that add value to these residues and simultaneously reduce the problems that are associated with their final disposal. The huge amounts of lignocellulosic biomass can potentially be used

Fig. 1 Lignocellulisc materials

to obtain heat power, and various values added biotechnological products, such as hydrogen, alcohol, olefins, gasoline, diesel, methane, oils, specialty chemicals, bioethanol, biodiesel, biobutanol, biohythane and others (Anwar et al. 2014; Akalın et al. 2017; Pérez-Rodríguez et al. 2018). Also, lignocellulosic waste has been used for the development of nanomaterials to biofuel production (Srivastava et al. 2017). In addition, after different conditioning treatments, lignocellulosic biomass can be used for the production of immobilized cell and enzyme systems. Immobilization on lignocellulosic wastes also allows reducing the disadvantages of using soluble enzymes.

Biomass can be classified in two ways according to the origin, function and final products. (1) Categorization based on types of biomass existing in nature, according to ecology or type of vegetation, which in turn divides into wood and woody biomass, herbaceous biomass, aquatic biomass, animal and human waste biomass, and biomass mixtures. (2) Categorization based on the use and application of biomass as feedstock (Tursi 2019). Herbaceous biomass is split into two main groups: energy crops, that have been exploited only in the bioenergy sector, and agricultural residues such as by-products of food, fibers or food industries (Tursi 2019). Typically, cell wall of agricultural lignocellulosic biomass is composed by cellulose (40–50% w/w), hemicellulose (10–25%) and lignin (20–30%), plus a small number of extractive solids and ashes (Anwar et al. 2014), although the content ratio of the biopolymers depends on the feedstock.

Cellulose is a natural semicrystalline polysaccharide that is widely abundant and present in the form of fibers of different sizes, from 0.5 to several mm. It is composed of β-D-glucopyranose subunits linked by highly resistant β-1,4-glycosidic bonds that can reach several thousand glucose units in length, with the levels together forming the spiral mode of a three-layer cell wall structure that forms the cellulose fiber (Anwar et al. 2014; Saha et al. 2016). Cellulose chains aggregate together in the form of elementary fibrils approximately 3 nm in diameter and can aggregate into larger micro- or macrofibrils. Cellulose nanofibers have been isolated from natural lignocellulosic sources, such as wood, banana peel, eucalyptus, kenaf, corn stalk, pine, jute, palm, grass, etc. (Alemdar and Sain 2008; Jonoobi et al. 2009; Uetani and Yano 2011; Besbes et al. 2011; Chen et al. 2011; Deepa et al. 2011; Jahan et al. 2011; Duan et al. 2013; Benhamou et al. 2014; Nakagaito et al. 2015; Zhu et al. 2016; Bondancia et al. 2017). Different processes, such as alkaline chemical pulping, bleaching, enzymatic hydrolysis and TEMPO oxidation, are used for chemical pretreatments of raw material. These processes are applied to separate fiber by dissolving lignin and hemicellulose (Rahmati et al. 2010; Chen et al. 2011; Jahan and Rahman 2012; Pouyet et al. 2013; Khalil et al. 2014b; Boufi et al. 2016). Other methods, such as high-pressure homogenization, microfluidization, microgrinding, high-intensity ultrasonication, electrospinning and steam explosion, are used as isolation treatments (Kim and Park 2006; Spence et al. 2011; Khalil et al. 2014a, 2016; Sulaiman et al. 2015a). Cellulose fibers, along with packaging, paper and coating, electronics, membranes, nanocomposites, textile and other industrial applications, have been widely used in various fields (Reddy and Yang 2005; Erdman et al. 2016; Khalil et al. 2016).

Techniques of immobilization

The selection of one adequate technique for immobilization plays a very important role in determining the activity of the biocatalyzer and the characteristics of the system. Factors such as cost of the immobilization procedure, enzyme deactivation and regeneration, toxicity of reagents, and final properties of the system must be considered for process specification and for selecting the immobilization technique (Mohamad et al. 2015). The immobilization of biocatalysts can be separated into two categories: chemical and physical methods. In the chemical method, covalent or ionic bonds form, while the physical method employs techniques that mainly involve hydrophobic or van der Waals interactions. The most commonly applied techniques for immobilization of cells and enzymes are adsorption, entrapment or inclusion, covalent binding and cross-linking. Systems with immobilized cells are less vulnerable to changes in the environmental condition, such as pH modification, and offer protection against toxic compounds.

Adsorption

The adsorption process is assessed by the direct submersion of the support in a medium containing an enzyme or cell. The attachment of the enzyme or the adhesion of microbial cells on surfaces is mainly carried out through van der Waals forces, ionic and hydrophobic interactions and hydrogen bonds. The adsorbed enzymes are protected from aggregation, proteolysis and interaction with hydrophobic interfaces (Datta et al. 2012). However, under industrial conditions involving high reactant and product concentrations, physical adsorption is generally too weak to keep enzyme fixed on the support (Sheldon 2007). Even so, immobilization of enzymes and cells by adsorption on lignocellulosic supports has been used successfully for the synthesis of products such as bioethanol, xylitol, hydrogen, fructooligosaccharides (FOS), acetone, butanol and others (see Tables 1 and 2). In solid supports with low loads of enzymes or cells, there is an excess of surface area, which means that the biocatalyst tends to maximize its contact with the support and spreads across the surface, which leads to its inactivation. To increase the adsorption efficiency, the tendency of the

Table 1 Lignocellulosic materials that have been used for the immobilization of enzymes

Enzyme	Raw material	Pretreatment	Immobilization method	Activation agent/spacer arm	Application	References
Candida antárctica lipase	Cashew apple bagasse	Cashew apple bagasse was washed with water, dried at 60 °C for 24 h and milled. Afterward, the bagasse was treated with alkaline hydrogen peroxide (4.3% v/v H_2O_2 at pH 11.5).	Covalent binding	Glycidol ethylenediamine Glutaraldehyde	Chemoenzymatic production of (R)-indanol	De Souza et al. (2016)
Candida antarctica lipase	Green coconut fibers	Green coconut fiber was cut and sieved to obtain particles between 32 and 35 mesh, washed with distilled water and dried at 60 °C	Adsorption	–	Processing, detergent formulations, and the synthesis of fine chemicals	Brígida et al. (2009)
Candida rugosa lipase	Wood cellulignin	Wood cellulignin was sieved to obtain particle sizes between 80 and 100 mesh and was neutralized with 0.1 M NaOH solution at a 1:15 (solid/liquid) ratio	Covalent binding	Glutaraldehyde carbonyldiimidazole	Hydrolysis and ester reactions	Gomes et al. (2005)
Candida rugose lipase	Rice straw	Rice straw was ground and sieved to obtain particle sizes between 80 and 100 mesh. This material was washed and dried at 100 °C	Covalent binding	Glutaraldehyde	Butyl butyrate synthesis	De Castro et al. (2001)
Candida rugosa lipase	Magnetic spent grain	Magnetic derivative of spent was washed and suspended methanol, and perchloric acid stabilized ferrofluid was added	Adsorption cross-linking covalent binding	Polyethylenimine Glutaraldehyde sodium periodate 1,4-butanediol diglycidyl ether	Supports for lipase immobilization	Pospiskova and Safarik (2012)
Lipase from Pseudomonas aeruginosa Maltogenic amylase from Aspergillus awamori var.	Corn stalks	Core was cut to a length of 10–20 mm, milled using a laboratory hammer mill and screened with a sieve shaker to ensure that the particle size was less than 1 mm	Adsorption	–	Production of adsorption materials from agricultural crop waste	Lv et al. (2013)

Table 1 (continued)

Enzyme	Raw material	Pretreatment	Immobilization method	Activation agent/spacer arm	Application	References
Laccase from *T. versicolor*	Green coconut	The fibers were dried at 60 °C, cut and passed through a 20-mesh screen. The coconut fibers were soaked with H_2SO_4 (v/v)	Covalent binding	Glycidol ethylenediamine Glutaraldehyde	Clarification of apple juice	Bezerra et al. (2015)
Laccase from genetically modified Aspergillus	Beer spent grain	Raw material was washed with distilled water and dried at 60 °C	Covalent binding	Glycidol ethylenediamine Glutaraldehyde	Fermentation processes Pulp delignification dye decolorization and contaminated water or soil remediation	Da Silva et al. (2012)
Laccase from Trametes versicolor	Pecan nut shell, peach stone, pistachio shell and pine nut shell	The lignocellulosic wastes were collected, milled and sieved to obtain a particle size of ~ 1 mm	Adsorption	–	Decolorization of aqueous solutions containing acid orange	Ramírez-Montoya et al. (2015)
Laccase from Trametes versicolor	Pine bark, nutshell, hazelnut shell, wood pallet	Each substrate was autoclaved at 120 °C during 30 min	Adsorption	–	Degradation of pharmaceutically active compounds (PhACs)	Torán et al. (2017)
Invertase from Saccharomyces cerevisiae	Wood chip, wood sawdust, wood shavings	Sawdust was autoclaved at 1.5 atm for 15 min without any treatment	Adsorption	–	Continuous sucrose hydrolysis in column bioreactor	Mahmoud (2007)
β-d-fructofuranosidase invertase,	Hydrophilic cotton, filter paper, multipurpose cloth, sugar cane bagasse, string, or gauze	One gram of the support was hydrated with 100 mL distilled water, and the pH was adjusted to 2.0 for 30 min under roller agitation (50 rpm)	Adsorption Cross-linking	Polyethyleneimine Glutaraldehyde	Stabilization and production of fructooligosaccharides	Gonçalves et al. (2015)
Horseradish peroxidase (HRP)	Cellulose fibers, microgranular cellulose (MCC)	Rayon filament yarn was ground to 0.26 mm arithmetic average length or 0.35 mm length.	Adsorption	–	Adsorption behavior and inactivation of HRP	Di and Yan (2009)
Glucoamylase	Bagasse dialdehyde cellulose	Cellulose fibers from bagasse were oxidized by sodium periodate in sulfuric acid media	Covalent binding	Sodium periodate	Supports for glucoamylase immobilization	Varavinit et al. (2001)

Table 1 (continued)

Enzyme	Raw material	Pretreatment	Immobilization method	Activation agent/spacer arm	Application	References
Trypsin	Spent grain	Dry spent grains (100 g) were mixed in a 1500 mL 3% (v/v) HCl solution at 60 °C for 2.5 h. The mixture was cooled and washed with water.	Covalent binding	Glycidol Ethylenediamine Glutaraldehyde	Establish an efficient protocol for trypsin immobilization	Rocha et al. (2011)
Tripsin	Corn cob powder	Lignol process with fast decompression and alkali treatment.	Covalent binding	Glycidol Ethylenediamine Glutaraldehyde	Peptides with bioactive potential from whey protein	Bassan et al. (2016)
Acid protease	Carbon derived from rice bran	Activated carbon was precarbonization and treated by chemical activation	Adsorption	–	Supports for protease immobilization	Kumar et al. (2009)
Rennin	Wood sawdust	Wood sawdust was treated with NaOH at 80 °C for 3 h to obtain tubular cellulose	Entrapment	–	Feta-type cheese production	Barouni et al. (2016)
α-amylase from Bacillus circulans	Coconut fibers	Coconut fibers were separated and boiled in water containing sodium dodecyl sulfate, followed by drying at room temperature	Adsorption	–	Supports for immobilization	Dey et al. (2002)
Xylanase and Peroxidase	Activated carbón from Soybean hulls	A solution at a 1: 1 mass proportion (salt/raw material) was pyrolyzed in a tubular oven, under a N_2 flow of 150 mL min^{-1}, at 550 °C, for 3 h	Adsorption	–	Novel eco-friendly biocatalyst	Torres et al. (2017)

Table 2 Lignocellulosic materials that have been used for the immobilization of cells

Cell/yeast	Raw material	Pretreatment	Immobilization method	Application	References
Saccharomyces cerevisiae	Wood chips (WC)	WC (7–10-mm-long and 1–2 mm thick) were filled evenly into a jacketed glass column	Adsorption	Develop a cost-effective continuous process to increase the productivity of lignocellulosic ethanol	Harde et al. (2014)
Saccharomyces cerevisiae	Wood shaving cane bagasse, corn leaf, corn cob	The materials were previously prepared for the experiments by applying washing processes with boiling water, drying at 105 °C, and achieving a mechanical reduction of size by using a blade mill (3.4–10 mm)	Adsorption	Improve the continuous production of ethanol in packed-bed reactors	Agudelo et al. (2012a)
Saccharomyces cerevisiae	Wine-making residues (grape pomace) Grape seeds, skins, stems, corn cobs	Grape pomace: Separation of seed, skin and stems. Seeds: natural form. Skins: crushed Corn cobs: Ground and sieved	Adsorption	Ethanol production	Genisheva et al. (2011)
Saccharomyces cerevisiae	Orange peel	Orange peel was cut into small pieces of 1–1.5 cm and sterilized at 120 °C for 15 min	Adsorption	Alcoholic fermentation and for fermented food applications	Plessas et al. (2007)
Saccharomyces cerevisiae	Bagasse (sweet sorghum stalk)	Raw material was chopped into small particles and dried and sieved	Adsorption	Ethanol production	Yu et al. (2010)
Saccharomyces cerevisiae	Maize stem disks	Maize stem disks were placed into an Erlenmeyer flask containing 0.9% NaCl solution	Entrapment	Ethanol production	Vučurović and Razmovski (2013)
Saccharomyces cerevisiae	Wood, shavings cane bagasse, corn cobs, corn leaves	Raw materials were subject to a conditioning process that involved cleaning, drying and size reduction	Adsorption	Ethanol production	Agudelo et al. (2012b)
Saccharomyces cerevisiae	Spent grains	Dry spent grains were mixed with an HCL solution at 60 °C for 2.5 h. The mixture was cooled, washed with water and dried. The remaining solids were partially delignified with NaOH at 30 °C for 24 h	Adsorption	Ethanol production	Brányik et al. (2001)
Saccharomyces cerevisiae	Pinewood chips	Raw material was treated with a sequential treatment of H_2SO_4 followed by sodium sulfite and sodium chlorite	Adsorption	Ethanol production	Dhabhai et al. (2012)

Table 2 (continued)

Cell/yeast	Raw material	Pretreatment	Immobilization method	Application	References
Clostridium acetobutylicum	Wood pulp, loofa sponge, coconut fibers, wood chips, and sugarcane bagasse	Materials were washed with water three times and were dried in an oven at 70 °C The wood pulp was distributed evenly on plastic mesh, rolled and put into a jacketed glass column	Adsorption	Production of acetone, butanol, ethanol	Survase et al. (2012)
Clostridium acetobutylicum	Coconut fibers coal (burned)	The supports were processed into 2–3 mm in size; their raw sources were further washed and dried in an oven at 60 °C and, finally, were sterilized by autoclaving at 121 °C for 15 min	Adsorption	Butanol production	Tripathi et al. (2010)
Clostridium beijerinckii	Oil palm shells, palm press fibers, empty fruit bunches, oil palm fronds	Each material was reduced and washed thoroughly with tap water and then dried at 70 °C	Adsorption	Solvent production: acetone, butanol, ethanol, acetic acid and butyric acid	Loyarkat et al. (2015)
Clostridium beijerinckii	Corn stalk	The corn stalk was then soaked with hydrochloric acid, and the slurry was placed in a 100 °C. The treated stalk was washed and dried at 80 °C	Adsorption	Solvent production: acetone, butanol and ethanol	Zhang et al. (2009)
Candida guilliermondii yeast	Sugarcane	Sugarcane bagasse was grounded and sieved. Washed, dried at 100 °C and sterilized (1 atm, 20 min) The bagasse was soaked in a 2% (w/v) NaOH solution	Adsorption	Production of xylitol	Silva et al. (2007)
Candida shehatae TISTR5843	Palm pressed fiber (PPF) Delignified PPF (DPPF)	PPF: sun-dried, milled and sieved DPPF: PPF + $NaClO_2$—ratio 10:1 (w/w). Soaked in 0.01% acetic acid solution at 70 °C for 1 h	Adsorption	Improved bioethanol production	Riansa-ngawong et al. (2012)
Enterobacter cloacae	Rice straw, bagasse coir		Adsorption	Hydrogen production	Kumar and Das (2001a)
Enterobacter cloacae IIT-BT 08	Rice straw, bagasse coir	The raw material was sterilized and the tubes were used for transportation	Adsorption	Continuous hydrogen production	Kumar and Das (2001b)

Table 2 (continued)

Cell/yeast	Raw material	Pretreatment	Immobilization method	Application	References
Aspergillus japonicus ATCC 20236	Brewer's, spent grain, wheat straw, corn cobs Coffee husks Cork oak, loofa sponge	They were boiled for 10 min, washed three times with distilled water and then dried overnight at 60 °C. Prior to use, all of them were autoclaved at 121 °C for 20 min	Adsorption	Production of fructooligosaccharides (FOS) and β-fructofuranosidase (FFase)	Mussatto et al. (2009)
Lentinula edodes CCB-42	Loofa sponges	Used loofa sponges were obtained from the dried fruit of Luffa operculate	Adsorption	Biosorption of the synthetic dyes Congo red, Bordeaux red and methyl violet	Gregolin et al. (2014)
Kluyveromyces marxianus	Banana leaf sheath pieces	The leaf sheath was cut and treated with 0.01 N NaOH solution at 120 rpm for 30 and were sterilized at 121 °C for 20 min before use	Adsorption	Ethanol production	Du Le et al. (2013)
Pichia stipitis	Sorghum stalks	Peeled sorghum stalks were sectioned into small pieces and autoclaved at 120 °C and were dried at 45 °C	Entrapment	Ethanol production	Gajula et al. (2011)
Fungus Trametes pubescens laccase	Sunflower-seed shells	Raw material was autoclaved at 121 °C for 20 min before use	Adsorption	Decoloration of metal-complex dyes	Rodríguez-couto (2014)
Bacillus pumilus HZ-2	Sugarcane bagasse	The bagasse was dried and mechanically comminuted into powder, washed and dried at 100 °C	Adsorption	Bioremediation of mesotrione-contaminated soils	Liu et al. (2015)

biocatalyst to leach must be suppressed, although it could be prevented by covalent binding (Sheldon and Woodley 2018).

Covalent binding

Covalent binding is a technique that has been researched extensively for coupling biocatalysts to insoluble matrices. Covalent links can form between functional groups of the support and functional groups of the amino acid residues in the biocatalyzer. Normally, in this technique, the enzyme is coupled with the previous activation of the functional groups on the support, thus making it a stronger electrophilic for a posterior reaction with some nucleophilic groups in the biocatalyzer such as $–NH_2$ from lysine or arginine, –COOH from aspartic and glutamic acid, –OH from serine and threonine and, –SH from cysteine. The reaction is followed by the elimination of excess biomolecules and reagents (Sassolas et al. 2012). At the end, the enzyme is tightly fixed on the support, the lixiviation is reduced, and the product is not contaminated with the enzyme. Covalent immobilization involves several reaction procedures, such as a peptide bond, diazotization, amino bond, Schiff's bases formation, thiol-disulfide, amidation reaction and alkylation (Sulaiman et al. 2015b). Generally, covalent immobilization is preferred in aqueous solutions and when there are factors of denaturation in the medium (Hanefeld et al. 2009). Enzyme immobilization by covalent binding has several advantages, e.g. little leakage of enzyme from the support during catalysis because of the tight binding, and typically improves the stability of the system (Varavinit et al. 2001). Some authors have used natural supports, such as cashew apple bagasse, wood cellulignin and spent grain, for successful immobilization through the covalent binding of Candida antarctica lipase, Candida rugosa lipase and trypsin (see Table 1), among others.

Cross-linking

The immobilization of enzymes by cross-linking is executed by simple precipitation of the enzyme from an aqueous solution, such as the physical aggregates of protein molecules, by the addition of salts, water miscible organic solvents or nonionic polymers (Homaei et al. 2013a). This technique is also applicable to the preparation of cross-linked enzyme aggregates containing two or more enzymes for use in one-pot, multistep syntheses (Sheldon et al. 2009). The most commonly used cross-linker is glutaraldehyde because it is inexpensive and easy to obtain in commercial quantities, although other cross-linkers, such as dextran polyaldehyde, are used when glutaraldehyde exhibits poor results (Sheldon and Van Pelt 2013). Few works have been published in relation to immobilization on lignocellulosic material by cross-linking. Some of those studies are mainly focused on the immobilization of enzymes, such as invertase and *β-d*-fructofuranosidase for the hydrolysis of sucrose and the stabilization and production of fructooligosaccharides, respectively (see Table 1).

Entrapment or inclusion

Direct immobilization of biocatalysts by physical entrapment into hydrogels or inside of fibers is applicable for purified enzymes and crude cell extracts. There are two types of material that are commonly used for enzyme immobilization by entrapment: hydrophobic materials and hydrophilic materials; the latter is useful because of its ability to keep large amounts of enzyme and its capacity for activity retention There are different methods of entrapment, such as temperature-induced gelation, polymerization by a chemical/photochemical reaction, and ionotropic gelation of macromolecules with multivalent cations (Asgher et al. 2014). In cell immobilization by entrapment, they are captured within a support matrix, which offers protection of cells from external aggressions (Bouabidi et al. 2018).

Carriers

Matrix characteristics play an important role in obtaining an efficient immobilized system. The differences in the morphological and physical–chemical characteristics such as pore size, hydrophilic/hydrophobic balance and surface chemistry of the support can affect enzyme immobilization, its catalytic properties, the stability and yield of the system (Mohamad et al. 2015). So, the performance of immobilized biocatalyst is tightly regulated by the material properties of the carriers (Verma et al. 2019). These are basic properties for the correct selection of an immobilization carrier: resistance to microbial and chemical degradation, the availability of a reactive functional group, preservation of physical integrity during the process and recycles, insolubility and inertness toward the reaction medium, a high diffusion coefficient and a superficial area. In addition, the carrier must be available in high quantities and must be affordable (Santos et al. 2005; Silva et al. 2007). For selection of the support material, factors to consider are the following: the nature of the bonds as covalent, noncovalent or different types of covalent or noncovalent bonds, the amount of bonds that form between the enzyme and the support, and the degree of confinement of enzymatic molecules in the support. The microenvironment and the condition of the system (pH, temperature) also have great importance (Cao 2005; Mohamad et al. 2015). In this regard, the optimal supports should have characteristics such as a hydrophobic or hydrophilic character, surface charges, surface functionalization, good

chemical and mechanical stability, high surface area, porosity and the proper particle size (Hanefeld et al. 2009).

Biocatalytic production holds great potential for clean and selective production processes. Enzymes are readily biodegradable, and generally after their use in industrial production, they have lower or null toxicity (Raman and Henning 2013). The materials that are used in the manufacture of the immobilization support can be natural polymers, such as alginate, chitosan and chitin, collagen, carrageenan, gelatin, cellulose, starch, pectin and Sepharose, synthetic polymers, such as ion exchange resins, polyvinyl chloride, polyurethane microparticles, polyvinyl alcohol and polyaniline, and inorganic materials, like zeolites, ceramics, Celite, silica, glass, activated carbon and charcoal (Datta et al. 2012; Morin-Crini et al. 2019). Recently, several types of carriers have been developed, such as magnetic nanoparticles, e.g., microspheres of various biomaterials and copolymers with magnetic particles; novel nanoparticles, e.g., gold nanoparticles, polyurethane microspheres-gold nanoparticles, palladium nanoparticles and zeolite-gold nanoparticles, and nonmagnetic nanoparticles, e.g., nanoparticles, nanotubes, nanoporous matrices and nanofibers (Ansari and Husain 2012).

Immobilization of enzymes and cells

Enzymes immobilization

Enzymes are readily biodegradable and generate lower global waste during the obtainment of products and at the end of processes. Additionally, enzymatic process meets the demands of green chemistry for industrial processes (Velasco-Lozano et al. 2018). Enzymatic catalysis has been implemented in a broad range of industries in recent years due to its specificity, fast action and often savings in raw materials, chemicals and/or water compared to those of traditional processes, and they are perceived to work under environmentally friendly conditions (Raman and Henning 2013).

In enzyme immobilization, the mobility of an enzyme is limited by the means of electrostatic or material barriers that separate it from the reaction medium, but the enzyme is still able to interact with target molecules from reagents and products (Rangel et al. 2011). Some advantages of enzyme immobilization are: (1) the product can be separated easily from the medium reaction; (2) stability of the reaction (under different pH and temperature conditions, solvents, and controlled impurities and contaminants) is improved; and (3) their stability could be enhanced depending on the enzyme, the method of immobilization and the type of support (Kim and Park 2006; Khalil et al. 2014a). Consequently, the use of immobilized enzymes greatly simplifies the design of the reactor and the control of the reaction (Mateo et al. 2007). The cost of the carrier is one of the most important criteria by which to consider processes at the industrial level; this, in combination with interest in the reuse of by-products, has led to a search for cheap and widely available carriers (Silva et al. 2007). Taking into account the above-mentioned conditions and criteria, lignocellulosic biomass meets the requirements for the selection of an optimal carrier in the immobilization process.

Wood from sawdust and shavings, coproducts from the rice industry, such as husk, straw, and hull ash carbon from rice bran, and derivatives from fruit processing, such as coconut fibers, cashew apple and bagasse, are waste that are commonly used in the immobilization of enzymes. System enzyme-waste has been used in processes such as the decolorization of aqueous solutions, pulp delignification, dyes and contaminated water or soil remediation, detergent formulations, the synthesis of fine chemicals, and pharmaceuticals. Some of the most used enzymes to develop biocatalytic systems waste-enzyme are:

Lipase

Nowadays, lipases have gained a lot of importance in the area of organic synthesis. However, the inactivation of lipase by organic solvents is often a problem (Kajiwara et al. 2019). Immobilization of lipase has allowed obtaining more thermostable and stable systems, as the reported by De Souza et al. (2016) to immobilization of lipase by covalent binging on cashew apple. In that case, the catalytic system was most stable in the presence of organic solvent for the production of (R)-indanol than the soluble lipase. Techniques as mass balance, chemical composition (FTIR), coupling yield (hydrolysis of olive oil), and catalytic activity in nonaqueous medium allow validating the selection of active biocatalysts (Gomes et al. 2005). Some authors have reported the biocompatibility of residues as wood cellulignin, coconut fibers, corn stalks, and spent grain to immobilization of lipase (Gomes et al. 2005; Brígida et al. 2008; Lv et al. 2013). Gomes et al. (2005) reported a biocatalytic system composed of wood cellulignin-lipase with similar or better characteristics than the natural and synthetic polymers, such as chitin and styrene–divinylbenzene copolymer. Lignocellulosic biomass as spent grain was modified with magnetic nanoparticles, and this novel technique allowed obtaining a biocompatible magnetic carrier for lipase immobilization. This system proposed by Pospiskova and Safarik (2012) presented stability much higher than the free enzyme. Biocatalytic system kept at least 80% of the enzymatic activity during 30 days, while the free enzyme just kept 8% of its initial activity after the same period of evaluation. These studies show that lignocellulosic materials are an interesting tool for immobilization of lipases. They have shown good stability

and reusability, being a promising low-cost biocatalytic applicable in fields as food technology and biotechnology.

Laccase

Laccase has large number of potential applications in biotechnological fields due to its different biological roles as lignin degradation, pathogenicity, detoxification morphogenesis and sporulation. For that, it is very used to prevent fruit juices & wine decoloration, detoxification of environmental effluents, oxidation of synthetic dye, among others (Singh and Gupta 2020). Clarification of juice has been widely studied, being immobilization of enzymes a novel alterative for the reuse of the enzyme. Bezerra et al. (2015) studied the use of coconut fibers (CF) as carrier to immobilization of laccase. They found that the combination of CF-laccase with thermal decompression and alkaline treatment, both allow producing and active and stable system, capable of efficiently oxidizing phenolic compounds to apple juice clarification. Also, Da Silva et al. (2012) reported that the catalytic systems conformed by spent grain-laccase was a successful biocatalyst to pulp delignification, dye decolorization and contaminated water. The authors, after kinetic parameters examination, found that the immobilized laccase on spent grain after acid and alkaline treatments had a much higher affinity and velocity for ABTS than the laccase immobilized on spent grain without chemical treatments. This is likely due that the alkaline digestion opens the structure of the remaining cell walls in the raw material, increasing the availability of functional groups for immobilization (Brányik et al. 2004). Laccase can be also immobilized by adsorption to degradation of pharmaceutically active compounds, as the reported by Torán et al. 2017 (Torán et al. 2017). The authors worked with pallet wood in a fluidized bed-reactor, and they achieved a favorable removal of ibuprofen, ketoprofen and naproxen from flocculated hospital wastewater after 49 days of operation. These results show that immobilized laccase can be used to confront the pollutants and environmental challenges, and others fields of waste management.

Other enzymes

Invertase is an enzyme that catalyzes the hydrolysis of the glycoside bond of the sucrose molecule to obtain an equimolar mixture of monosaccharides (Gonçalves et al. 2015). Much of the biochemistry processes that involve invertase are focused on yeast fermentations and processes for conversion of starch to sugar. The use of lignocellulosic materials has played an interesting role to immobilization of invertase to hydrolysis sucrose and production of fructooligosaccharides. Gonçalves et al. 2015 tested a wide variety of lignocellulosic waste with low-cost and biodegradable characteristics, such as hydrophilic cotton, filter paper, multipurpose cloth, sugar cane bagasse, string, or gauze as carrier to immobilization of invertase. They obtained higher yield of immobilization by using filter paper and string. In addition, the authors found that all the carriers tested were more stable than the free enzyme, indicating a good enzyme stabilization and a good production of stable derivatives. Also, biocompatibility of trypsin was tested in spent grain and corn cob powder, to establish an efficient protocol to immobilization and to production of bioactive peptides, respectively (Rocha et al. 2011; Bassan et al. 2016). Authors found that the retention of activity depends of the grade of purity of the enzyme and that it is possible to obtain hydrolyzates from cheese whey and catalytic systems with higher activities. Table 1 summarizes some of the lignocellulosic materials that have been reported as support to the immobilization of enzymes.

Cells immobilization

Immobilization of cells has been a well-known practice in the alcoholic beverage industry since the end of the last century. The immobilization of cells can be done by adsorption or entrapment, but immobilization by passive adhesion to surfaces is more preferred due to limited problems related to diffusion (Survase et al. 2012). Cells immobilization has many advantages, such as a large number of easily available catalysts, which lead to an eventual increase in the efficiency and productivity of the process, the formation or production of secondary metabolites coupled to growth, the application of anchorage-dependent cells that grow only when they are attached to surfaces, and the ease of catalytic system recovery from the medium reaction (Varavinit et al. 2001; Homaei et al. 2013b). In addition, when cells are immobilized by adsorption, they offer direct contact between nutrients and the immobilized cells, which minimizes the diffusion problems (Zhang et al. 2009). Also, the systems developed offer other advantages, such as lower susceptibility to contamination by other microorganisms, less vulnerability to the toxic substances that are present in the bulk phase and protection against pH changes, which makes the cells more tolerant to environmental changes (Harde et al. 2014; Zur et al. 2016). However, the immobilization of cells presents disadvantages, such as limited volumetric activity, difficulty in predicting changes in cellular growth, and physiological and metabolic activity mass transfer limitation due to cellular growth in the catalyst matrix (Agudelo et al. 2012b; Bornscheuer et al. 2012). System cell-waste has been used mainly in alcoholic fermentation of several carbohydrate substrates like glucose, molasses, xylose, raisin extracts, to obtain solvents such as butanol, ethanol, acetone, acetic acid

and butyric acid. Some of the most used cells to develop biocatalytic systems waste-cells are:

Saccharomyces

Strains of *Saccharomyces cerevisiae* have been used for many years to produce fermented foods and beverages. It is the most used microorganism for the production of bioethanol from biomass (Favaro et al. 2019). Traditional ethanol fermentation is produced by free or immobilized cells. In the process with free cells, the batch bioreactor is filled with the culture medium and cells, at the end of fermentation; the fermented medium is removed from the bioreactor. While fermentation with free cells implies a decrease in productivity due to the process of filling and emptying of the bioreactor, fermentation with immobilized cells allows obtaining enhanced biological stability, higher biomass concentrations and higher process productivity (Vučurović and Razmovski 2013; Harde et al. 2014). For that, in a continuous fermentation process, cell immobilization is preferred because it facilitates the purification of extracellular products (Li et al. 2014). The use of lignocellulosic materials for *Saccharomyces Cerevisiae* immobilization has been demonstrated to be an interesting alternative to ethanol production, as reported by Genisheva et al. (2011) to wine elaboration by using grape skins and corn cobs. They found that the amount of cells immobilized into untreated grape skins and corn cobs was higher than that obtained to the same treated materials. Authors noted that the immobilization did not occur in a homogeny form on the material structure. It is because rough and porous structures favored cells adhesion. However, this not implies that the ethanol concentration has to be proportional to the concentration of immobilized cells, but it has the advantage that the reuse of the support provides a higher ethanol productivity (Genisheva et al. 2011).

Clostridium

Clostridium is widely used as a natural producer of biofuels and bulk chemicals. Some authors have reported the use of lignocellulosic materials to immobilization of *Clostridium* (see Table 2). Loyarkat et al. (2015) evaluated the production of solvents by using palm tree wastes to *Clostridium beijerinckii* immobilization. They found that the oil palm fronds were the most suitable support for cell immobilization and that the operation of two-stage fermentation was optimal for production of solvents with a high yield. On the other hand, Survase et al. (2012) worked with several agricultural residues to immobilization of *Clostridium acetobutylicum*. They obtained a process cost-effective, promoting a successful concept of wood-based bio-refinery, in which pulp produced in the process of making sugar mixture was used as carrier to cells immobilization. As can be seen, one of the most attractive properties of using lignocellulosic biomass as support to immobilization of cells is that in some cases, the materials can be sent back to the hydrolysis process, as in the case of sugar production, which minimizes waste generation (Zhang et al. 2009).

Other microorganisms

Although *Saccharomyces cerevisiae* is the preferred microorganism to ethanol production, its growth is slightly reduced around 35 °C. However, authors have evaluated the production of ethanol at temperature from 40 to 45 °C by using immobilized cells with the ability to assimilate sugar under high temperatures (Du Le et al. 2013). In another way, ethanol production by yeast cells immobilization has some technical barriers, which can be overcome with a correct selection of porous materials to immobilization (Gajula et al. 2011). Other systems' cell-waste has been evaluated with biotechnological and bioremediation purposes, as the continuous production of hydrogen and fructooligosaccharides, and mesotrione biodegradation. Table 2 summarizes some of the lignocellulosic materials that have been reported as support to the immobilization of cells.

Immobilization on cellulose nanofibers

Nanocellulose or cellulose nanofibers (CNF) have several properties, such as a high aspect ratio, a low density, a very low coefficient of thermal expansion and a high tensile strength. Moreover, they exhibit some excellent properties for enzyme immobilization, including a high number of functional groups on the surface support. Depending on the production process, CNF can present different forms, such as suspensions, powders, films, hydrogels and aerogels or nanofibrous membranes (Nechyporchuk et al. 2015; Mishra et al. 2018). Nanocellulose plays an important role in biotechnologies fields, mainly in few emerging areas, including enzyme immobilization, flexible electronics, modeling of cellulosic, among others. Enzyme immobilization on cellulose derivatives, such as cellulose acetate and carboxymethyl cellulose, has been widely studied (Santos et al. 2005; Gajula et al. 2011), although it has not been efficiently studied on CNF without modifications. For instance, Sulaiman et al. (2015a) studied the development of a matrix for covalent binding immobilization of cyclodextrin glucanotransferase from *B. macerans* on CNF from kenaf by using an alkaline process and high-intensity ultrasonication as the raw material pretreatment. On the other hand, Mahmoud et al. (2009) studied the development of a matrix for the covalent binding immobilization of cyclodextrin glycosyl transferase and alcohol oxidase on a nanocomposite of cellulose nanocrystal

from flax/gold nanoparticles; finally, Sathishkumar et al. (2014) immobilized laccase on cellulose nanofibers by covalent binding to simulate a dye effluent treatment.

Lignocellulosic waste pretreatment

Generally, biomasses can have physical and/or chemical modifications. A pretreatment step is required to increase the affinity between the carrier and the biocatalyst, thereby improving the effectiveness of immobilization. Physical pretreatments are carried out by size reduction, washing and simple sterilization using higher temperature and pressure to remove impurities and dirt (Jørgensen and Pinelo 2017). While chemical treatments involve the use of the reagents such as sodium hydroxide, sulfuric acid, hydrochloric acid, and hydrogen peroxide, among others. HCl is usually used to activate the surface of the carrier by removing the wax and destroy hemicellulose (Zhang et al. 2009). On the other hand, hydrolysis with alkaline solution is used to remove lignin by saponification of intermolecular ester bonds (hemicelluloses-lignin) (Bassan et al. 2016). In addition, a combination of high temperatures with organic solvents promotes intramolecular hydrolysis of lignin, disruption of intermolecular ester bonds, and promotes the hydrolysis of glycoside bonds of hemicelluloses (Bassan et al. 2016). In fact, the use of these treatments makes the support more porous and increased the superficial area, which creates an environment that improves immobilization. Tables 1 and 2 show some of the pretreatments used to raw material conditioning.

Functional group activation

Different chemical agents react with functional groups on the support; however, the treatments that are used require high care and selection of the appropriate parameters to carry out the reaction in the system. In a covalent interaction, it is important to use chemical coupling agents, such as ligands and spacer arms, since these can improve binding efficiency and minimize the steric hindrance to provide greater mobility. Cellulose fibers or nanofibers present great potential for covalent immobilization due to their good mechanical properties, and they are rich in hydroxyl functional groups that can be activated or modified by the use of specific reagents (Sulaiman et al. 2015b). Several protocols of activation by using agents such as 1,4-butanodiol diglycidyl ether, carbonyldiimidazole, cyanogen bromide, and 3-aminopropyltriethioxysilane, have been reported. These have been used for insertion by chemical coupling of a reactive hydroxyl group, which leads to the formation of activated groups, such as amino, carboxyl and epoxy groups, that can react with amine groups from enzyme (Gomes et al. 2005; Schaubroeck et al. 2010; Eldin Mohy et al. 2011; Wang et al. 2011; Sun et al. 2012; Elschner and Heinze 2015; Homaei 2015; Manoel et al. 2015; Zhang et al. 2016; Lou et al. 2017; Sharifi et al. 2018; Jiménez-Meneses et al. 2019). Also, lignocellulosic supports are converted into anion exchangers through contact with reagents as polyethyleneimine (Gonçalves et al. 2015). As is well known, glutaraldehyde has been widely used as a cross-linker for stabilization of the enzyme and for changing the binding of functional groups of cellulose. It can also act as a ligand agent or spacer arm between the support and the enzyme, thereby preventing steric constraints (Rocha et al. 2011; Gunda et al. 2014; Bezerra et al. 2015; De Souza et al. 2016; Zhang et al. 2016). Table 3 summarizes some of the reaction mechanisms of the interaction of chemical coupling agents.

Conclusion

In search of developing environmentally friendly systems and aiming to solve the problem of waste storage and management, the use of lignocellulosic biomass as a support for immobilization is a very competitive alternative. Lignocellulosic materials encompass the characteristics an ideal matrix. Physical and chemical biomass modifications offer an ideal environment for immobilization. Immobilization on lignocellulosic materials is attracting the interest of the scientific community in different fields, such as chemical, pharmaceutical, biotechnology, food industry and environmental. In this context, lignocellulosic biocatalysts constitute a green route for the development of more sustainable bioprocesses.

Table 3 Chemical coupling of reactive hydroxyl group

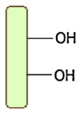
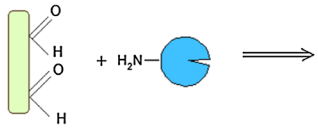
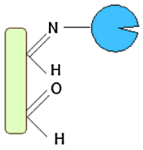
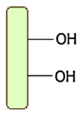
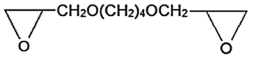
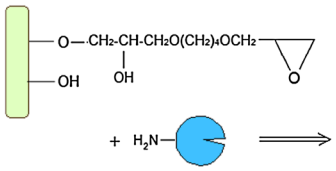
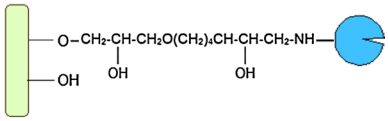
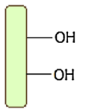
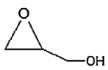
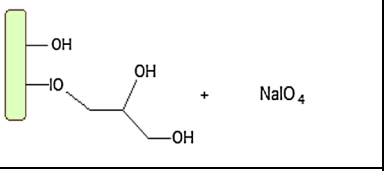
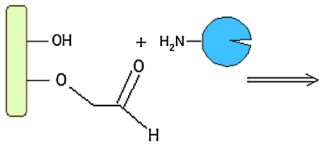
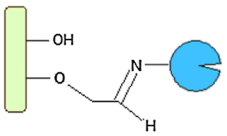
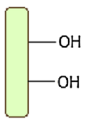
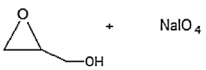
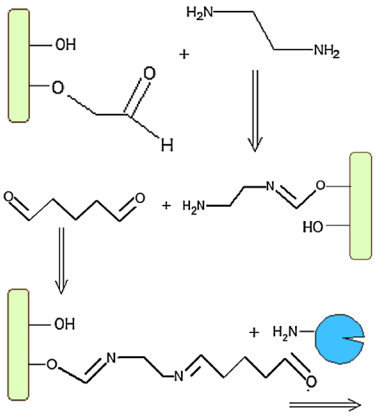
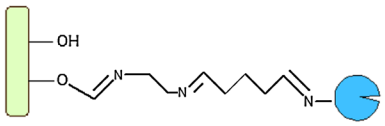
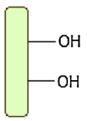
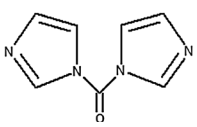
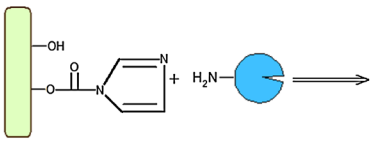
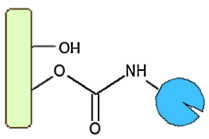
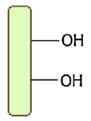
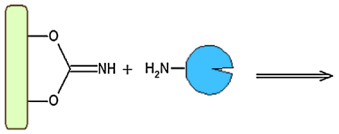
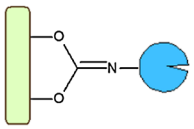
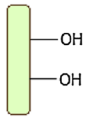
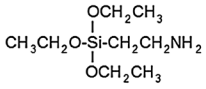
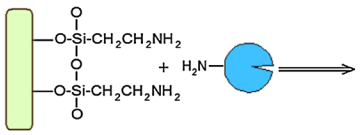
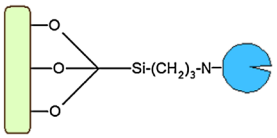
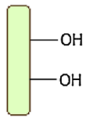
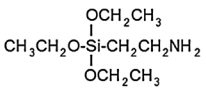
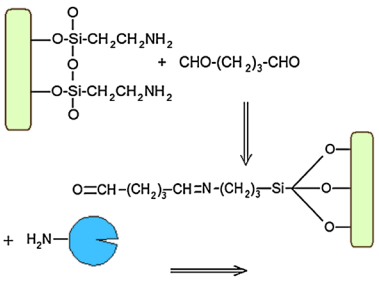
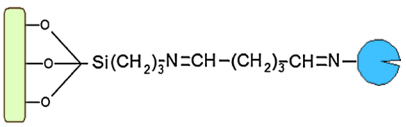
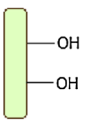
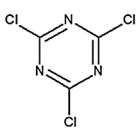
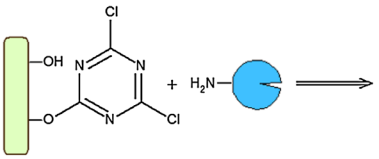
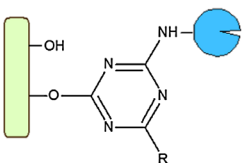
Hydrolyxl group	Protocol of activation (Ligand)	Active support + Enzyme	Immobilized enzyme
	 Sodium periodate		
	 1,4 butanodiol diglycidyl ether		
	 Glycidol	 Oxidation with $NaIO_4$ 	
	 Glycidol	 Ethylenediamine + Glutaraldehyde	
	 Carbonyldiimidazole		

Table 3 (continued)

Hydrolyxl group	Protocol of activation (Ligand)	Active support + Enzyme	Immobilized enzyme
	 Cyanogen bromide		
	 3-aminopropyltriethioxysilane (APTES)		
	 APSTES (Space arm)	 Glutaraldehide (Ligand)	
	 Trichlorotriazine (Cyanuric chloride)		

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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