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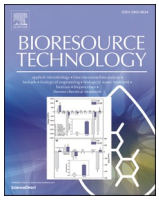

Sustainable enzymatic treatment of organic waste in a framework of circular economy

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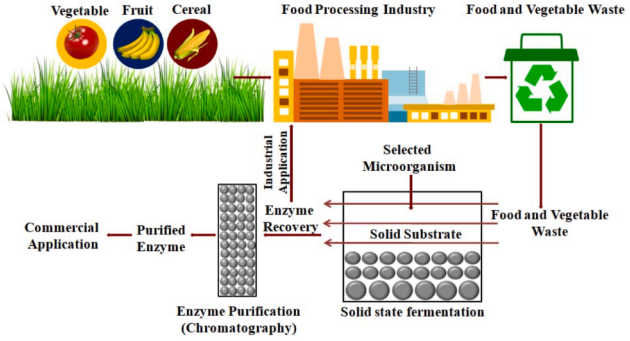
HIGHLIGHTS

- Role of enzymes for food and vegetable waste valorization was evaluated.
- Industrial, exo and endo enzymes, whole cell bioconversion processes were reviewed.
- Valuable byproducts from enzyme treatment of FVW were discussed.
- Life cycle of enzymatic food and vegetable waste valorization was assessed.
- Integrated biorefinery supporting circular economy was presented.

GRAPHICAL ABSTRACT



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ABSTRACT

Enzymatic treatment of food and vegetable waste (FVW) is an eco-friendly approach for producing industrially relevant value-added products. This review describes the sources, activities and potential applications of crucial enzymes in FVW valorization. The specific roles of amylase, cellulase, xylanase, ligninase, protease, pectinase, tannase, lipase and zymase enzymes were explained. The exhaustive list of value-added products that could be produced from FVW is presented. FVW valorization through enzymatic and whole-cell enzymatic valorization was compared. The note on global firms specialized in enzyme production reiterates the economic importance of enzymatic treatment. This review provides information on choosing an efficient enzymatic FVW treatment strategy, such as nanoenzyme and cross-linked based enzyme immobilization, to make the process viable, sustainable and cheaper. Finally, the importance of life cycle assessment of enzymatic valorization of FVW was impressed to prove this approach is a better option to shift from a linear to a circular economy.

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1. Introduction

The alarming amount of food waste (FW) produced throughout the food supply chain and its effects on the depletion of natural resources have drawn attention worldwide. Globally, around 1.3 billion tonnes of food and vegetable waste (FVW) get accumulated annually, and by 2025, this number is expected to rise to 2.2 billion tonnes (FAO report, 2019). Approximately $ 680 billion and $ 310 billion are accounted for food loss in developed and developing countries, respectively (Melikoglu et al., 2013; FAO report, 2019). Regarding FW, India ranks seventh, with the Russian Federation at the top (Dahiya et al., 2018). FVW represents the most significant type of biogenic waste entering landfills which emits greenhouse gases and causes adverse environmental impacts. FVW generation's repercussions have raised the urgency to investigate and develop comprehensive strategies to solve the global FVW generated during the last decade. The well-known methods of processing FVW are combustion, gasification, composting and anaerobic digestion (AD), which are discussed in Section 3. The AD is the most advantageous method because it treats waste and produces energy with an energy recovery potential of about 250 kW per tonne of FW. However, the hydrolysis of particulate organic matter in FVW having cellulose crystallinity and lignin barrier remains challenging for several biological processes, including AD, necessitating a longer retention time (Chakraborty and Venkata Mohan, 2018; Chakraborty and Venkata Mohan, 2019). Although traditional pretreatment methods such as mechanical (heat), chemical (acid-alkali) and physicochemical (integrated heat-acid-alkali) increase the fermentation efficiency of FVW, they are expensive, require significant water, and produce inhibitory chemicals such as 5-Hydroxymethyl furfural and aldehyde (Schroyen et al., 2014).

In this context, biological and enzymatic pretreatment techniques are attractive because they enable better bioresource recovery from FVW than established conventional technologies since they are more specific, require less chemical and energy input, and do not generate any process inhibitors (Schroyen et al., 2014). The pretreatment of FVW using pure microbial enzymes is expensive. Alternatively, employing crude enzymes from biomass lysate for pretreatment can be economical (Kiran et al., 2014). The key players in enzyme-mediated depolymerization of FVW are ligninases, proteases, carbohydrases, lipases and pectinases, which systematically cleave the particulate matter of the FVW composed of lignin, lipids, proteins, holocellulose, pectins into simpler subunits (Fig. 1). Hydrolyzed FVW can further be converted into biofuels and platform chemicals through AD and other biological processes (Chatterjee and Venkata Mohan, 2022; Kiran et al., 2014; Ravindran and Jaiswal, 2016). Hence, the food supply chain must integrate systematic practices with enzymatic FVW conversion technologies to achieve sustainable FVW management.

Though enzymatic procedures have an advantage over other biomass-degrading technologies, whole-cell mediated bioconversion of FVW is favoured because it allows for direct microbial action on FVW. Significant research is being conducted to enhance microbial bioconversion utilizing various wild-type or engineered microorganisms (Ravindran and Jaiswal, 2016; Patria et al., 2022). However, a new generation of enzyme production technologies is needed to hydrolyze the complex biomolecules in biomass at a lower cost. Simultaneously, enzymatic bioconversion technologies can be made economically viable by producing high-titer in-house enzymes boosted by providing the most favourable circumstances with minimum capital investment. Hence, the goal is to propose an innovative enzyme-based FVW valorization model to generate value-added products to enable a self-sustaining economy and environmental remediation within the context of the circular economy. The shift to a circular bio-economy will help to provide economic development and employment generation.

In light of this, the current review seeks to thoroughly examine the

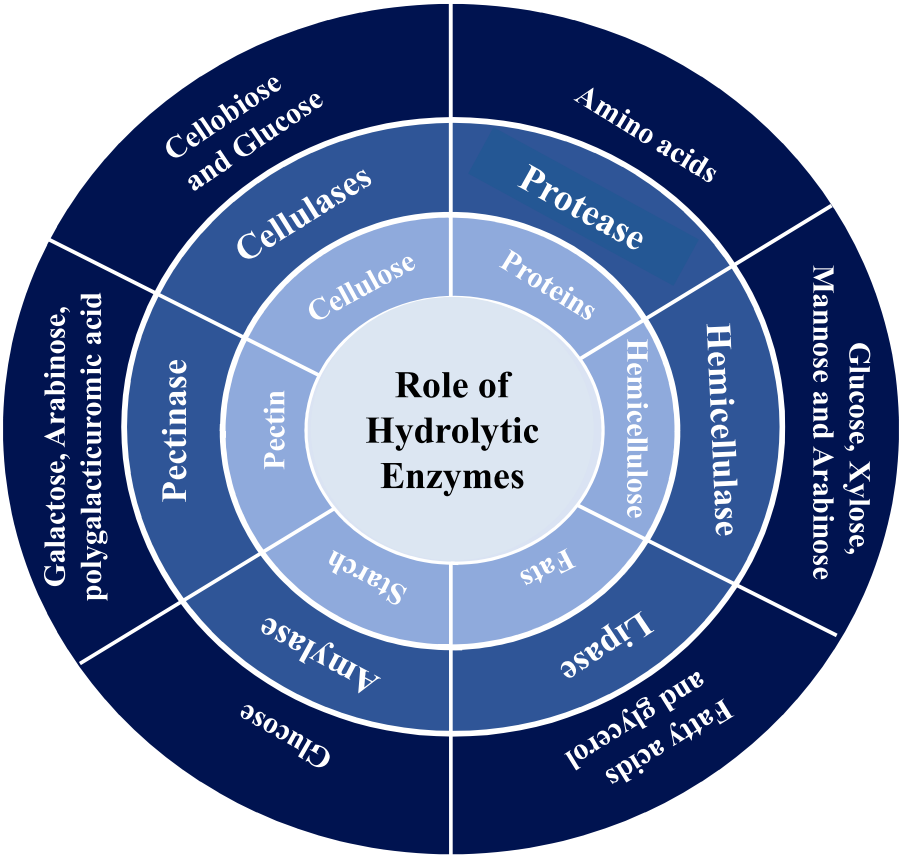

Fig. 1. Synergistic effect of hydrolytic enzymes during pretreatment of food and vegetable waste.

major enzymes involved in FVW treatment, their industrial uses, and the essential sustainability-compliant measures. The review's first section elaborates on the advantages of enzymatic pretreatment models over traditional pretreatment techniques. The role of industrial enzymes in FVW treatment and their sources, including bacteria, yeasts, and fungi, are discussed. Also, the mechanism of enzymatic pretreatment techniques of naturally occurring exo and endo enzymes, whole-cell bioconversion processes, and their prospects for converting FVW to value-added products in the linear and circular economies are elucidated. Finally, this review guides selecting a cost-effective enzymatic method for valorizing bio-commodities from FVW in the circular economy perspective.

2. Physical and biochemical composition of FVW

To the annual global FVW production, India contributes about 30 % to grains, 40 % to 50 % to root crops, fruits, and vegetables, 20 % to meat, dairy products, and oil seeds, and 35 % for fishes. The highest rate of FW is contributed by fruits, vegetables, roots, and tubers (FAO report, 2019). Based on the reliable FW characteristics, a statistical survey of the FW carried out in South Asia, including China, for one year suggested that FW is composed of 50 % fruits, 20 % starchy food, 20 % vegetables, and 10 % meat. However, FW generated from these regions typically contain 35-50 % fruits and vegetables, 20 % meat, 30 % fish and seafood, and 20 % dairy products (Ravindran and Jaiswal, 2016; FAO, 2019).

FW consisted of 10-16 % solids, 10-40 % lipids, 3.9-21.8 % proteins, 80–90 % volatile solids with a C: N ratio of 13.2–36.4 and volatile solids (VS): total solids (TS) ratio of 0.80–0.97 (Karthikeyan et al., 2016). Characteristics of FW explained by many researchers showed that FW contains 17–23 % reducing sugars, 30–34 % starch, and 2–14 % fibre on a w/w basis (Zhang and Richard, 2011; Moon et al., 2009). Table 1 represents the characteristics of FW, which vary depending on the generation source.

The majority of waste generated by food processing industries is lignocellulosic and their heterogeneous aromatic structure is composed of phenolic monomers such as coniferyl alcohol (guaiacyl propanol), coumaryl alcohol (p-hydroxyphenyl propanol) and sinapyl alcohol (syringyl alcohol) (Althuri et al., 2017). Plant-based FW are high in starch, xylan, mannan, pectin, tannin, and other nutrients. Particle size, moisture, VS and nutrient contents greatly influence the extraction of high-value components and energy recovery from FVW, which require specific treatment technologies. Conventionally landfilling, composting, thermal treatment and AD technologies are followed for the FVW treatment.

3. Conventional strategies for FVW valorization

The landfill bioreactor is one of the most simple, cheap, and efficient ways to dispose waste, particularly in nations like the EU and the US. However, uncontrolled open decomposition of FVW dramatically contributes to global warming and reduces the ability to recover resources. FVW is an excellent substrate for composting because of its high organic content. The FVW's organic matter is converted into a stable, nutrient-rich soil component through an aerobic biodegradation process that uses oxygen, nitrate, and sulphate as electron acceptors. The C: N ratio of the substrate is crucial for the composting process. Altering the substrate, C: N ratio and adding additives and appropriate inoculum improve the efficiency and quality of composting (Wang et al., 2022). Compost made from FVW has an excellent nutritional balance, making it suitable for horticultural and agricultural uses.

Common thermal techniques used for FVW treatments include incineration, gasification, and pyrolysis. FW is burned during the incineration process to produce heat energy and ash by being exposed to combustion in the presence of air. According to Caton et al. (2010), incinerators can reduce the amount of FVW by 85 %, so they are widely used in nations with a shortage of landfill space. However, the FVW's high moisture content and potential for dioxin emissions make the incineration process undesirable. Thermal treatment of FW containing more than 70 % moisture is inefficient because significant energy is used to dry the substrate, raising doubts about the process's dependability and efficacy (CIWEM, 2013). Utilizing combustion as a different FVW management technique allows for direct energy recovery from FVW (Caton et al., 2010). When FW is burned, a significant amount of chemical energy may be obtained. Once the water is removed from FVW, it can be made into pellets and used for co-firing with coal in boilers.

The most practical method for digesting organic waste, including FVW, to generate renewable energy as an alternative to fossil fuels is AD. Single-stage AD of FVW by Leach-bed reactor (LBR) and liquid waste by Continuously Stirred Tank Reactor (CSTR) are well-known methods to recover acids and methane (Chakraborty et al., 2018, Chakraborty et al., 2022). Recent developments have been made in utilizing FVW through a two-stage AD process. The first stage involves hydrolysis and acidogenesis, which produces volatile fatty acids; during the second stage of methanogenesis, acetate is converted to methane (Chakraborty et al., 2022). Methane enrichments were performed by directing the off gas from the acidogenic reactor to the methanogenic reactor, where acetoclastic methanogenesis and hydrogenotrophic methanogenesis also occur (Yan, 2016). However, for FVW, enzymatic pretreatment before AD helps efficient resource recovery by enhancing sugar release from the complex lignocellulosic components.

4. Important enzymes in FVW valorization

AD technology is favourable for carbohydrates and starch-rich organic waste, but FVW contains varying amounts of lignin which restricts depolymerizing enzymes' access to the carbohydrates in the organic waste. Lignin makes bioprocessing of FVW challenging by

Table 1
Biochemical composition of food waste generated in various countries.

Country	TN (%)	TCH (%)	VS/TS	TC (%)	S (%)	H (%)	C/N	Reference
India	1.1	24	0.89	40	0.1	7.29	36.4	Yan, 2016
Korea	2.8–5.2	2.55	0.89–0.94	47.8–51.2	0.7	6.1–7.7	18.3	Yan, 2016
USA	2.8–2.95	2.5	0.86–0.94	51.2	0.8–0.7	7.2	18.3	Yan, 2016
China	2.56	NA	0.91	48.3	NA	6.91	18.9	Chang. and Hsu, 2008
Japan	3.4–4.2	6–7.2	0.89–0.92	42.3	NA	6.1	13.2	Chu et al., 2008
Taiwan	3–4	NA	NA	50–52	NA	NA	15	Forster-Carneiro et al., 2008
Spain	1.5	NA	0.86	55.5	NA	NA	37	El-Mashad and Zhang, 2010.
Hong Kong	4.5	74	0.97	53	NA	NA	11.7	Yan, 2016
Thailand	4.8–5.1	NA	2.4	46.3–44.8	0.11–0.15	5.03–5.21	9.21	Tuprakay et al., 2014
Canada	2.4–6.7	NA	NA	NA	NA	NA	20.5	Opatokun et al., 2015
England	3.32	5.3	1.1	54.9	0.25	6.9	16.54	Yirong et al., 2017

NA-not available, TN-Total nitrogen, TCH-Total carbohydrate, TC-Total carbon, VS-Volatile solid, TS-Total solid, C/N-carbon to nitrogen ratio, S-Sulphur, H-Hydrogen.

intricately binding with cell wall carbohydrates (cellulose and hemicellulose) and forming a rigid shield of the lignin-carbohydrate complex that acts as a physical barrier (Althuri et al., 2017). Lignin also initiates non-specific interactions with hydrolytic enzymes that reduce the net available free enzyme systems for hydrolysis (Li et al., 2016). Thus, accessing cellulose, xylan, hemicellulose, and lignin requires breaking down the lignin-carbohydrate complex for which pretreatment techniques are needed, which aid in the bioconversion of lignin-rich feed to value-added platform chemicals. Compared to other physical, chemical and mechanical pretreatment techniques, bio-based processes are eco-friendly and economical because they have lignin-specific enzymatic action, low inhibitor formation and hemicellulose loss, high sugar recovery, mild reaction conditions, and no toxic waste streams produced (Schroyen et al., 2014).

Complex organic molecules convert into simple molecules with the help of extracellular enzymes during FVW hydrolysis. For example, complex polysaccharides such as starch, cellulose and cyclotetraglucose are converted to simple sugars (C_6), hemicelluloses are broken down into C_5 (arabinose, xylose) and C_6 (glucose, galactose, mannose) sugars and proteins (aleurone and albumin) are broken down into amino acids. Lipids are transformed into fatty acids and glycerol, as depicted in Fig. 1 and Table 2. The extracellular enzymes such as proteases (from *Bacillus* sp.), amylases, cellulases (from *Cellulomonas* sp.), hemicellulase (from *Trichoderma reesei*), lipases (from *Mycobacterium* sp.) catalyze the reactions mentioned above (Kiran et al., 2014). Significant research was performed to optimize the bioconversion of FVW by targeting different types of wild-type (e.g., *Trametes trogii*, *Pleurotus ostreatus*) or engineered microorganisms (*Trichoderma orientalis* EU7-22) (Seiboth et al., 2011). Since lower enzyme loading techniques help develop cost-effective processes, it is essential to maintain extensive information on the source, their mechanism, and the application of extracellular enzymes to optimize enzyme loading and substrate selection. Therefore, the following subsections, together with Table 2, cover the categorization, source, mechanism, and applications of typical FVW degrading enzymes. Being rich in polysaccharides, lignocellulosic FVW waste material is an obvious choice of raw material for producing lignocellulose-degrading enzymes, which is discussed in the following subsections.

4.1. Amylases

Long-chain saccharides are broken down by α, β and γ amylases (Table 2; Fig. 2). Amylase enzymes (EC 3.2.1.1), which are derived from thermophilic microorganisms, are resistant to extreme pH and chemical reagents, have a longer shelf life and have fewer contamination issues, which has triggered interest in the exploration of thermophiles (Rani et al., 2015; Msarah et al., 2020). The cost of producing α-amylase can be reduced by using solid-state fermentation (SSF) and substituting agro-industrial wastes and FVW for expensive substrates (Tiwari et al., 2015). Table 2 (1) and Fig. 2 (1) provides a detailed description of various types of amylases.

4.2. Cellulases and xylanases

After proteases and amylases, cellulase (EC 3.2.1.4) is the third most used enzyme in the industry for depolymerizing cellulose to glucose monomer units, as shown in Fig. 2 (2). Microbial extracellular cellulases that have been studied extensively in bacteria or fungi are given in Table 2 (2). The genome of the fungus *Trichoderma reesei* contains the genetic codes for 10 cellulases and 16 hemicellulases. Anaerobic cellulolytic bacteria bind to the substrate through cellulosomes on the cell surface. The substrate then undergoes supramolecular restructuring, causing the cellulosomal subunits to redistribute and interact with the many target substrates (Kuhad et al., 2011).

The two main enzymes that hydrolyze xylan, the main constituent of hemicellulose, are endoxylanases (EC 3.2.1.8) and β-xylosidases (EC 3.2.1.3) (together termed xylanases) as presented in Table 2 (3) and Fig. 2 (3). In many industrial applications, the synergistic activities of cellulases and xylanases are necessary since cellulose is not present alone but is found in lignocellulosic fibres together with lignin and hemicellulose (Bajaj and Mahajan, 2019). Cellulase and xylanase are primarily derived from fungi, including *Trichoderma* and *Aspergillus* species, for industrial usage, including FVW treatment. Many wild (*Bacillus amyloliquifaciens*; *Clostridium stercorarium*; *Pseudomonas* sp.; *Nocardiopsis* sp. KNV) and engineered strains (*Yarrowia lipolytica*; *Trichoderma orientalis* EU7-22) have been reported for synergistic enzyme activities used in biomass saccharification, bioethanol production and agro-waste treatment (Bajaj and Mahajan, 2019).

4.3. Ligninases

Ligninases (EC 1.11. 14) are a group of oxidoreductive enzymes that find their application as lignin-modifying enzymes such as phenol oxidases, lignin peroxidases, manganese peroxidases, and versatile peroxidases. Ligninases are produced by fungal species belonging to white-rot, soft-rot, and brown-rot type wood-decaying fungi. White-rot fungi (*Basidiomycetes* and *Ascomycetes*) are the most efficient in degrading carbohydrates and lignin (Janusz et al., 2017). Phenol oxidases include catechol oxidases, monophenol monooxygenases, laccases, cresolases, and monophenol oxidases. These enzymatic systems degrade lignin and increase the average pore size and available surface area for easy access to hydrolytic enzymes (Althuri et al., 2017).

4.3.1. Lignin peroxidases

Lignin peroxidases (LiP), one of the effective oxidoreductases with EC 1.11.1.14, can cleave both phenolic and non-phenolic portions of lignin, as presented in Table 2 (4.1). These *N*-glycosylated enzymes are heme-containing proteins having a prosthetic group made of iron protoporphyrin. An overall two-step reaction involving (i) the radical cation oxoferryl unstable intermediate compound I formation and (ii) the neutral oxoferryl intermediate compound II formation constitutes the LiP-catalyzed hydrolysis process (Janusz et al., 2017). Due to their higher redox potential, these enzymes can oxidize a wide range of reducing substrates that are lignin analogs, and their broad applicability is presented in Table 2 (4) (Kumar and Chandra, 2020). Fungi-mediated SSF on lignocellulosic substrates such as rice straw, wheat straw, banana trash, corn cobs and FVW may produce LiP at a low cost which can be recovered through solid–liquid separation. The LiP produced will be stable over a wide range of temperatures (35–55 °C) and pH (1–5) (Falade et al., 2017; Althuri et al., 2017).

4.3.2. Manganese peroxidases

Manganese peroxidases (MnP) (EC 1.11.1.13) are heme-containing *N*-glycosylated proteins that oxidize lignin, related compounds and non-phenolic compounds in an H_2O_2-dependent manner, similar to LiP, Table 2 (4.2) (Kumar and Chandra, 2020). MnP can be produced through SSF using lignin-rich organic wastes such as rice straw, banana waste, corn cobs, sawdust and FVW or via submerged fermentation (Falade et al., 2017). This enzyme is stable over a wide pH (2.5–6.8) and temperature (30–60 °C). However, due to the low enzyme titer and yield obtained, industrial use of this enzyme is limited, and attempts were made to improve the titer by developing recombinant strains.

4.3.3. Laccase

Laccases (EC 1.10.3.2) (benzenediol: oxygen oxidoreductases) are ligninolytic enzymes produced extracellularly by many fungal species which have attracted broad industrial applications. The oxidation of substituted phenols, anilines, and aromatic thiols is catalyzed by the enzyme laccase, which contains four copper atoms and competes with molecular oxygen for the role of an electron acceptor. These enzymes have gained popularity as potential industrial enzymes because of laccase's capacity to cleave lignin's phenolic and non-phenolic subunits [Table 2 (4.3)]. Laccase enzymes are classified as Type 1 (blue), Type 2

Table 2
Classification, source, mechanism and application of key food and vegetable waste hydrolysing enzymes.

Enzyme	Classification and categories	Enzyme source	Mechanism of enzyme action	Uses and applications	References
1.Amylase	α-Amylases	Thermophilic microorganisms	1. Breaks long-chain saccharides to produce "limit dextrin" from amylopectin and maltotriose and maltose from amylose	1. Biocatalyst preparation, clinical, medicinal, analytical chemistry and molecular biology applications.	Rani et al., 2015; Msarah et al., 2020
	(1,4-D-glucan glucanohydrolase; glycogenase) (EC 3.2.1.1)	*(Bacillus amyloliquefaciens*, *B. licheniformis*, *B. subtilis*, and *B. stearothermophilus)*		2. Food, textile, and paper industries. 3. In distilleries and brewing industries	
	β-amylase (1,4-D-glucan maltohydrolase) (EC 3.2.1.2)	Seeds of higher plants and sweet potatoes	It operates from the non-reducing ends and cleaves off two glucose units (maltose)	1. Mashing and brewing process 2. Production of maltose-rich syrup	
	γ-amylase (glucan 1,4-α-glucosidase) (EC 3.2.1.3)	Plants and animals	Cleaves α (1–6) glycosidic links and the final α (1–4) glycosidic bond at the non-reducing ends	1. Less frequently used in the industry	
2.Cellulase	1.exo-(1,4)-β-D-glucanase (EC 3.2.1.91)	1. Fungi, bacteria, protozoans, plants, and animals. 2. Mainly in bacteria or fungal species such as *Aspergillus* sp., *Cellulomonas* sp., *Clostridium* sp., *Thermomonospora* sp., *Trichoderma* sp.	It acts on the cellulose chain's ends to produce β-cellobiose	Cellulase and xylanases are synergistically used in: 1. Pulp and paper	Kuhad et al., 2011; Sampathkumar et al., 2019
	2. endo-(1,4)-β-D-glucanase (EC 3.2.1.4)		It acts on the interior O-glycosidic linkages resulting in glucan chains of various lengths	2. Textile and laundry	
	3. β-glucosidases (EC 3.2.1.21)		It selectively acts on the β-cellobiose disaccharides to release glucose	3. Biofuel, food and feed 4. Brewing and agriculture industries	
3.Xylanases	Endoxylanases (EC 3.2.1.8) and β-xylosidases (EC 3.2.1.37)	1. Filamentous fungus (main commercial supplier), 2. Bacteria (*Bacillus megaterium*, *B. stearothermophilus* SDX, etc.), yeast, marine algae, protozoans, insects, and seeds.	Endoxylanases break down the homopolymeric backbone of 1,4-linked β-D-xylopyranose to release xylooligomers, which are then dissociated by β-xylosidases to give xylose.		Dhiman et al., 2008; Kamble and Jadhav, 2012
4. Ligninases	1. Lignin peroxidizes (LiP) (EC 1.11.1.14)	Fungal species: *Fomes lignosus*, *Lentinus degener*, *Phanerochaete chrysosporium*, *Peniophora gigantea*, *Phlebia brevispora*, *Phlebia radiata*, *Pleurotus sajor-cajo*, *Polyporus osteiformis*, *Pycnoporus sanguineus*, *Trametes hirsuta* and *Trametes versicolor*	1. This enzyme disintegrates β-O-4 ether and biphenyl bonds and then performs one-electron oxidation to generate free cation radicals.	1. Biorefineries, textile industry, bioremediation, cosmetic industries, and dermatological applications	Janusz et al., 2017; Kuahr et al., 2007; Maciel et al., 2010; Kumar and Chandra, 2020
			2. These radicals engage in hydroxylation or C—C bond breaking, to generate hydrophilic by-products	2. Production of value-added products such as 1-butanol, bio-methane, bio-hydrogen, organic acids, xylitol, microbial polysaccharides and single-cell protein	
		Bacterial species: *Acinetobacter calcoaceticus* and *Streptomyces* sp.	3. This enzyme also delignify non-phenolic lignin in hydrogen peroxide in a LiP-independent manner to propagate the free radical reaction via polymerization reaction, side-group deletion and rearrangement mechanism		
	2. Manganese peroxidizes (MnP) EC 1.11.1.13	Several bacteria, basidiomycetes, white-rot fungi, and algae. *(Agaricus bisporus*, *Phanerochaete laevis*, *Phlebia radiate*, *Pleurotus ostreatus*, *Pleurotus sajor-caju*, *Trametes hirsuta*, *Trametes versicolor*, *Lentinus tigrinus*, *Polyporus ciliates*, *Pycnoporus sanguineus*, *Physisporinus rivulosus*, *Ceriporiopsis subvermispora*, *Nematoloma frowardii*, etc.)	1. Oxidize Mn^{2+} to Mn^{3+} 2. Manganese ions chelates with the key redox intermediates to form the manganese oxide chelator complex. 3. The Mn^{3+} chelate complex diffuse into the enzyme's active site	1. Management of agricultural waste, 2G biorefineries 2. Degradation of complex pollutants (polycyclic aromatic hydrocarbons, nitro-aromatic compounds etc.) and bioremediation of industrial dyes.	Ayuso-Fernández et al., 2017; Xu et al., 2017; Althuri et al., 2017

(*continued on next page*)

Table 2 (*continued*)

Enzyme	Classification and categories	Enzyme source	Mechanism of enzyme action	Uses and applications	References
			4. This chelate complex further dignifies phenolic lignin by acting as a redox intermediate. 5. In the presence of H_2O_2 oxidant, MnP also catalyzes the oxidation of non-phenolic pollutants from Mn^{2+} to Mn^{3+}		
	3. Laccase EC 1.10.3.2	White-rot fungus: *Pleurotus ostreatus*, *P. djamor*, *Trametes versicolor*, and *Phlebia radiata*, *Phanerochaete chrysosporium* Basidiomycete: *Agaricus bisporus, Botrytis cinerea. Thelophora terrestris*, *Lentinus squarrosulus*, *Coprinus cinereus*, *Lenzites betulina*	1. Phenolic lignin oxidation occurs without mediators that form unstable phenoxy radicals. 2. That further proceed the reaction through a series of secondary responses such as hydration, disproportionation, or polymerization, resulting in Cα-oxidation, Cα-Cβ cleavage, and aryl–alkyl cleavage.	Due to the laccase's capacity to cleave lignin's phenolic and non-phenolic subunits, they are used in 1. Biorefineries	Chaurasia et al., 2013; Pannu and Kapoor, 2014; Kudanga and Roes-Hill, 2014
		Ascomycota: Red bread mould, *Neurospora crassa*	3. Non-phenolic lignin is oxidized in the presence of mediators (e.g., 1-hydroxy benzotriazole (HBT); capable of acting as an electron shuttle)	2. Food industry	
		Deuteromycetes: Trichoderma *longibrachiatum, T. harzianum, and T. atroviride*, Bacteria: *Bacillus subtilis*, *Azospirillium lipoferum*, *Streptomyces coelicolor*, *S. lavendulae*, *Marinomonas* sp.,	4. The oxygenated laccase diffuses into the non-phenolic lignin subunits and cleaves them	3. Pulp and paper industry 4. Cosmetics industry	
5. Pectinases	Pectinases EC 3.2.1.15	Various fungi, bacteria, yeasts, protozoans, insects, nematodes, and plant species. Fungus: *Aspergillus niger*, *A. japonicus*, *Penicillium canescens*, and *P. italicum*	1. Pectinases degrade the pectin complex by depolymerizing pectin with the help of hydrolase and lyase. 2. Pectin lyases catalyze the β-elimination reaction between two methylated residues, whereas polygalacturonases break the 1,4-glycosidic bonds between two galacturonic acid residues.	1. Paper and pulp industries 2. Textile industries	Zeni et al., 2011; Taskin, 2013; Garg et al., 2016
		Bacteria: *Bacillus macerans*, *B. pumilus*, and *B. subtilis* Yeast: *Rhodotorula glutinis* MP-10		3. Fruit and vegetable processing 4. Vegetable oil extraction 5. Fiber scouring from plant 6. Treatment of pectic wastewater and biorefinery industries 7. Tea-coffee fermentation	
6. Tannases	Tannases (Tannin acylhydrolases) EC 3.1.1.20	Bacteria: *Bacillus pumilus*, *B. cereus*, *Achromobacter* sp., *Corynebacterium* sp., *Klebisella planticola*, *Pseudomonas solanaceanum*, *Lactobacillus acidophilus*, *Enterococcus faecalis*, *Weissella* sp., *Leuconostoc mesenteroides*, and *Citrobacter* sp. *Fungus: Aspergillus niger*, *Penicillium notatum*, *Trichoderma viride*, *Fusarium solani*, *Paecilomyces variotii*	1. These are classified as serine esterases 2. It hydrolyze ester bonds like galloyl ester of alcohols and depside bonds, i.e., the galloyl ester of gallic acid present in complex tannins and related polymers to produce gallic acid moieties and glucose	1. Make gallic acid and propylgallate from tannins 2. Process tea, stabilize the colour and flavour of wine and coffee	Kumar et al., 2019; Aguilar et al., 2007; Govindarajan et al., 2016
		Yeasts: *Candida* sp., *Saccharomyces cerevisiae*, *Mycotorula japonica*, *Pichia* sp., and *Debaryomyces* sp.		3.Treat leather 4. Removing undesired tannins from fruit juices and beverages to improve quality and to reduce bitterness	
7. Proteases	1. Exopeptidases (Target site is one or two terminal amino acids of the peptide)	1. Plant protease such as bromelain, ficin, and papain are isolated from the plants *Ananas comosus*, *Ficus carica*, and *Carica papaya*	Serine proteases 1. Serine in the active site	1. Plant proteases used in the brewing, dairy, and pharmaceutical sectors	Souza et al., 2015; Razzaq et al., 2019 Mahajan et al., 2015; Badgujar et al., 2010

(*continued on next page*)

Table 2 (*continued*)

Enzyme	Classification and categories	Enzyme source	Mechanism of enzyme action	Uses and applications	References
	2. Endopeptidases (Target site is the middle of the peptide)	2. Animal protease trypsin, chymotrypsin, pepsin, and rennin are extracted from pigs and cows		2. Animal sources are used in the biocontrol of pests and for medical purposes	
	2(a) Serine proteases (EC 3.24.21)	3. Bacterial and fungal proteases are extracted from *Bacillus brevis*, *B. clausii*, *B. licheniformis*, *B. subtilis*, *Pseudomonas aeruginosa*, *P. putida*, *Serratia liquefaciens*, *Aromonas hydrophila*, *Aspergillus awamori*, *A. flavus*, *A. niger*, *Fusurium oxysporum*, *Rhizomucor* sp., *Phanerochaete chrysosporium*, *Trichoderma harzianum*, *T. reesei*, *Penicillium camemberti*, *Mucor circinelloides*, etc.	2. Broad substrate specificity, and high stability in extreme conditions	3. Bacterial and fungal proteases find broad range of applications in food, feed, dairy, tanneries, meat, brewing industries	
	e.g., Proteinase K, trypsin		3. Amidase and esterolytic activity	4. Cheese industries for ripening cheese; enhancing oil recovery from seafood; bread making and meat tenderization.	
	2(b) Aspartic acid proteases (EC 3.4.23)		Aspartic acid proteases	5. Wastewater treatment.	
	2(c) Cysteine proteases (EC 3.4.22)		1. Two reactive aspartic acid residues in the active site	6. Metalloproteases that have applications in drug development	
	2(d) Metalloproteases (EC 3.4.24)		2. Act on peptide bonds with non-polar amino acid	7. Threonine and glutamic acid proteases have applications in therapeutic management and food industries	
	E.g., Collagenase, thermolysin and dipase		Cysteine proteases		
	2(e) Threonine proteases (EC 3.4.25) (e.g., acyltransferases)		1. Constitute cysteine-histidine dyad in the active site 2. Reducing agents (DTT and EDTA) are required for initiating the catalytic reaction		
	2(f) Glutamic acid proteases (EC 3.4.23.32) (e.g., pepsin)		Metalloproteases 1. Required divalent metal ions, such as zinc, cobalt, and manganese 2. Sensitive to chelating agents Threonine proteases and glutamic acid proteases Have threonine and glutamic acid in the active site		
8. Lipases	Triacylglycerol acylhydrolases	1. Animal and insect lipases are produced by the human pancreas and gastric cells.	Substrate-specific lipases	1. Microbial lipases are used as biocontrol agents, in FVW treatment and in milk product, biosurfactant, wax, soap and biodiesel production	Chandra et al., 2020; Sarmah et al., 2018; Thakur, 2012
	(EC 3.1.1.3)	2. Plant lipases are mainly derived from seeds and beans such as sunflower seed, linseed, sesame, carica papaya, almond, barley, fenugreek, coconut, oat, and corn.	1. Selectively cleave the carboxylic ester bonds of lipid (fat) molecules into free fatty acids, and glycerol.	2. Plant lipases used in vegetable oil hydrolysis, structured lipid production.	
	a) Substrate-specific,	2. Bacterial lipases are derived from *Bacillus subtilis*, *B. pumilus*, B. *licheniformis*, *B. coagulans*, *Pseudomonas aeruginosa*, *Burkholderia multivorans*, *Burkholderia cepacia*, and *Staphylococcus caseolyticus*.	2. Capable of catalyzing esterification, interesterification, and transesterification processes	3. Animal lipases mostly have applications in clinical diagnosis.	
	b) Regio-selective	3. Fungal lipase producers are	Regio-selective lipases	4. Substrate-specific lipases used in biodiesel production and synthesis of high purity diaceylglycerols	
	i) 1,3 specific lipases	*Rhizopus arrhizus*, *Aspergillus sp.*, *Penicillium citrinum*, *P. simplicissimum*, *Geotrichum candidum*, *Colletotrichum gloesporioides*, and *Candida utilis mucilaginosa*, *Yarrowia lipolytica*, *Saccharomyces cerevisiae*,	1. Regio-selective lipases favour their activity depending on positional specificity	5. Fatty acid-specific lipases are applied in wastewater denitrification and in electricity, biodiesel and transportation fuel production.	

(*continued on next page*)

Table 2 (*continued*)

Enzyme	Classification and categories	Enzyme source	Mechanism of enzyme action	Uses and applications	References
		Aureobasidium pullulans, and *Williopsis californica*			
	ii) fatty acid-specific lipases		i) 1,3 specific lipases that hydrolyze the linkage between the C1-C3 position of triacylglycerols to form fatty acids, 2 and 1,3 or 2,3 mono and diacylglycerols	6. Enantioselective lipases are used in the conversion of secondary alcohol to pharmaceutical products and menthol benzoate to cosmetic and food products.	
	iii) Non-specific lipases and		ii) Fatty acid-specific lipases cleaved long fatty acid chain having a double bond at C9		
	c) Enantioselective		iii) Non-specific lipases catalyze the hydrolysis of triacylglycerols into free fatty acids and glycerol Enantioselective lipases 1. Can separate the enantiomers in a racemic mixture and catalyze the hydrolysis of one of the racemic mixture's isomers.		
9. Auxiliary Enzymatic Systems	1. Zymases	*Saccharomyces cerevisiae*	1. Zymases are capable to ferment a range of sugar monomers due to the presence of a group of enzymes, viz., invertase, hexogenase, isomerase, etc.	First-generation (1G) ethanol production from sucrose, starch etc.	Parapouli et al., 2020; Heckmann and Paradisi, 2020; Althuri et al., 2017
	2. Swollenins, and		2. Expansins strategically modify carbohydrates' compactness by breaking the hydrogen bonding within these structural polymers without directly solubilizing them.		
	3. Expansins		3. Swollenin mediate the swelling and weakening of fibers in carbohydrate moieties without releasing any detectable amounts of sugar monomers.		

(regular), and Type 3 (binuclear) copper based on UV/visible and electron paramagnetic resonance spectroscopy. The substrate's actual oxidation occurs in T1 copper, where the electrons are absorbed. Then the T2 and T3 coppers join to form a trinuclear cluster. At this location, oxygen is reduced into water molecules (Kudanga and Roes-Hill, 2014; Janusz et al., 2017; Curran et al., 2021).

Different microorganisms, such as fungi from the *Ascomycetes, Basidiomycetes*, and *Deuteromycetes,* that could grow on lignin-rich biomass produce laccases (Pannu and Kapoor, 2014) (Table 2). *Monocillium indicum* was the first identified laccase producer from *Ascomycetes* which showed peroxidase activity (Pannu and Kapoor, 2014). Laccases from bacteria and fungi are effective and stable at higher temperatures (60 °C), pH (6–8), and salinity (1-5 %). Laccases can be produced cheaply using lignin-rich organic wastes through SSF. The various types of non-edible/non-grazable lignocellulosic FVW that are abundantly available for laccase production include detoxified *L. camara* (red sage), *R. communis* (castor), *S. spontaneum* (wild sugarcane) and *Bambusa bamboos* (bamboo). Orange peels, grape seeds, wheat straw, sugarcane bagasse, coconut coir, rice bran, cotton stalk, and agricultural residues are other popular feedstocks for laccase production (Althuri and Venkata Mohan, 2019). In addition to the well-known ligninases and LiP, other lignin-degrading and accessory enzymes such as aryl-alcohol oxidase, aryl-alcohol dehydrogenase, glyoxal oxidase, and cellobiose dehydrogenase were also reported (Althuri et al., 2017).

4.3.4. Pectinases

Pectinases (EC 3.2.1.15) cleave complex pectic polysaccharides composed of repeating units of D-galacturonic acids found in plant cell walls. The most common pectinase and esterase are protopectinases, polymethyl galacturonase, pectin methyl esterases, pectin acetyl esterases, polygalacturonase, pectate lyase, and pectin lyase. Others include rhamnogalacturonan rhamnohydrolases, rhamnogalcturonan galacturonohydrolases, rhamnogalacturonan hydrolases, rhamnogalacturonan acetylesterases, and xylogalacturonan hydrolase (Janusz et al., 2017; Patidar et al., 2018). Pectin concentration in FVW is substantial and ranges between 2.8 % and 25.5 %. The concentrations of pectin in some of the FVW are citrus peel: 24.5 %, mango peel: 8.8 %, banana peel: 2.8 %, apple pomace: 12.5 %, carrot peel: 9 %, green beans cutting waste: 8.2 % (Christiaens et al., 2015).

Pectinases recovered from *Aspergillus* and *Penicillium* species show maximum activity in the acidic to neutral pH range. In contrast, pectinases of bacterial origin, viz., *Bacillus* sp., have pH and temperature optima in the alkaline range and within 40–75 °C temperature (Garg et al., 2016). Production of tannase and pectinase from free and immobilized yeasts *(Rhodotorula glutinis* MP-10) is simple, giving them an edge over filamentous fungi (Taskin, 2013). Pectinases have a growing market in the biotechnological sector and occupy the leading position in the market for industrial enzymes (Garg et al., 2016). Furthermore, applying pectinases and other carbohydratases in FVW processing can significantly enhance the recovery of total sugars.

4.3.5. Tannases

Tannases (EC 3.1.1.20), often referred to as tannin acylhydrolases, are a group of extracellularly secreted inducible enzymes that hydrolyze gallotannins, complex tannins, and gallic acid esters. Tannins are fundamentally secondary plant metabolites, and the complex-forming ability of tannins with other macromolecules is primarily caused by the presence of reactive phenolic hydroxyl groups (Govindarajan et al., 2016). The tannin content of FVW, such as pomegranate peel, spent tea powder, banana peel, tamarind seed powder, coconut coir, keekar leaves, and jamun leaves, lies in the range of 0.9–18.6 % (Nandini et al., 2013). Table 2 (6) discusses some tannase-producing bacterial, fungal,

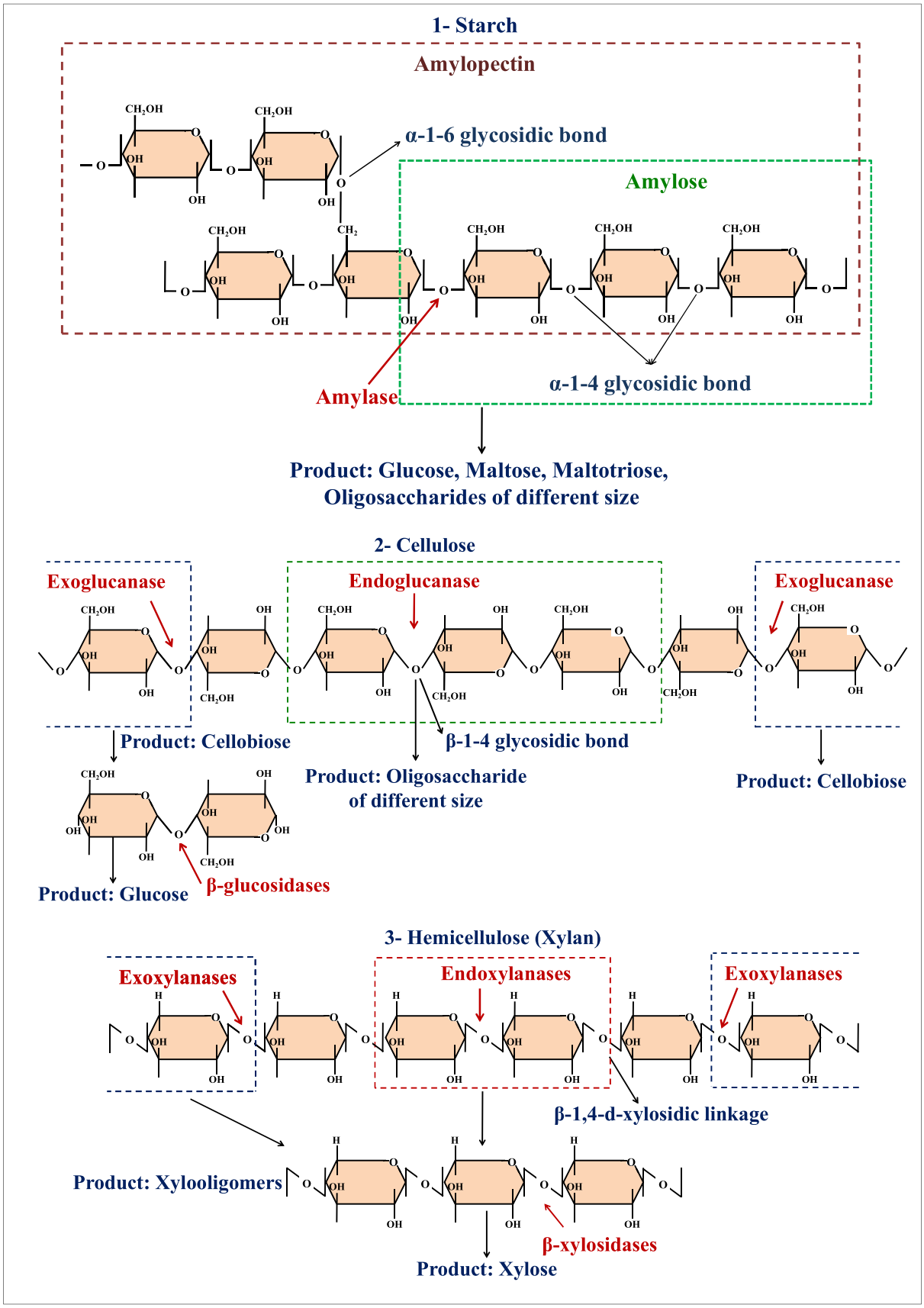

Fig. 2. Mechanism of action of hydrolytic enzymes on complex food and vegetable waste.

and yeast species, along with the mechanisms of action and applications. Tannases are suggested to be used in FVW processing along with other macromolecular depolymerizing enzymes for sustainable resource recovery.

4.4. Proteases

Protease, a hydrolytic enzyme, dissolves the peptide bonds in proteins. The global market value for proteases was about $ 2.21 billion in 2021, with a compound annual growth rate (CAGR) of 6 % from 2016 to 2021 (Razzaq et al., 2019). Exopeptidases and endopeptidases, two proteolytic enzyme groups, are classified depending on the place of action on the polypeptide chain. Based on the differences in the specific active site residues, endopeptidases are further divided into six groups: serine proteases, aspartic acid proteases, cysteine proteases, metalloproteases, threonine proteases, glutamic acid proteases. The different types of proteases and the mechanism of action and applications are presented in Table 2 (7). Proteases exhibited alkaline properties, with maximum protein (fish) solubilization ability at pH 7.5–9.5 and 50 °C. It was discovered that *B. megaterium* had the highest protein solubilization (30 %) compared to *A. hydrophila* (18 %) and *P. marinoglutinosa* (negligible), implying that protease-mediated waste protein treatment is feasible (Souza et al., 2015). Similarly, for FVW, with considerably high protein content, proteases can be used for effective feed hydrolysis because protein molecules play a physiological role through their interaction with carbohydrate moieties. Thus, enhanced sugar recovery and value-added product generation from FVW can be possible.

4.5. Lipases

Triacylglycerol acylhydrolases, known as lipases (EC 3.1.1.3), are hydrolases that selectively cleave the carboxylic ester bonds at the oil–water interface to break down lipids (fat) molecules such as triglycerides into diglycerides, monoglycerides, free fatty acids, and glycerol. These are applied in wastewater denitrification, electricity production, biodiesel transesterification, and fuel production. The lipid content of FVW ranges between 6.4 and 24.1 %, so lipases play a crucial role in FVW processing to produce value-added products (Paritosh et al., 2017). Industrial uses of lipases in the food, detergent, and pharmaceutical sectors are the most significant. Microbial lipases have attracted industrial attention because they are more stable, selective, and broad in their substrate specificity with simpler production and purification process than animal and plant lipases. These applications are possible due to the catalytic ability of lipases for many reactions, including hydrolysis, esterification, transesterification, deacetylation, alcoholysis, acidolysis, saponification, ethanolysis and hydrolytic kinetic resolution (Sarmah et al., 2018; Chandra et al., 2020). The details of lipases, including the sources, enzymatic mechanisms and industrial applications, are presented in Table 2 (8).

4.6. Other auxiliary enzymatic systems (Zymases)

Auxiliary enzymes such as zymases, swollenins, and expansins support the mainstream industrial enzymes for the bioconversion of numerous substrates, including FVW [Table 2 (9)]. Zymase found in yeast *Saccharomyces cerevisiae* catalyzes several reactions that convert sugars to alcohol. The optimal pH range for zymase is alkaline, and its activity is inhibited even in mildly acidic environments. At temperatures above 55 °C, this enzyme complex denatures (Parapouli et al., 2020). This enzyme can ferment a range of sugar monomers, such as dextrose, D-galactose, D-mannose, and laevulose, commonly present in FVW (Parapouli et al., 2020). Zymase is a comprehensive enzyme that plays a significant role in first-generation (1G) ethanol production from sucrose by converting it into glucose and fructose by invertase. Other enzymes of the zymase complex subsequently transform these sugar monomers into ethanol and carbon dioxide. Similarly, starch is converted to 1G ethanol by the zymase complex diastase, which acts on starch to release maltose, which is then converted to glucose by maltase. The enzyme then acts on free glucose molecules to produce ethanol and CO_2. Due to the potential of zymase, this complex could process FVW with high starch and sucrose content to recover value-added platform chemicals (Parapouli et al., 2020). Expansins and swollenins are different non-hydrolytic enzymes that assist carbohydrolases in depolymerizing polysaccharides. These specialized enzymes are utilized along with cellulases and xylanases for the efficient degradation of FVW (Althuri et al., 2017).

5. FVW conversion to value-added products

Valorizing FVW to bioenergy and value-added products supports maximum resource recovery and waste management. Being rich in carbohydrates, FVW can be subjected to various bioprocesses to produce biofuels and biobased products (Fig. 4). Bioethanol is a potential liquid biofuel that can be effectively produced from enzymatically treated FVW hydrolysate. For commercial production of bioethanol from FVW, some factors need to be considered, such as (i) pretreatment of substrate for removal of recalcitrant compounds and (ii) selection of effective hydrolysis method for maximum conversion of carbohydrates to fermentable sugars. There are numerous reports on bioethanol production from FVW. Chatterjee and Venkata Mohan (2021) reported thermal-assisted chemical pretreatment of different VW using 1 % H_2SO_4 (v/v) followed by enzymatic saccharification (using an enzyme cocktail of 100 IU amylase and 10 IU cellulase per gram VW), which yielded 0.251 g/g ethanol from sweet potato waste followed by yam waste (0.240 g/g) and potato waste (0.234 g/g). Onsite multienzyme produced by *Fusarium oxysporum* F3 under solid-state cultivation using wheat bran (WB) with amylase (17.8 U/g WB), glucoamylase (0.1 U/g WB), endoglucanase (65.2 U/g WB), b-glucosidase (27.4 U/g WB), cellobiohydrolase (3.5 U/g WB), xylanase (221.5 U/g WB), b-xylosidase (0.7 U/g WB) and total cellulase titers of 1.5 U/g WB, respectively were used to hydrolyze FW and subsequent ethanol production. The productivity of *F. oxysporum* monoculture was 0.17 g L^{-1} h^{-1} with a bioethanol production of 16.3 g L^{-1}, but with *F. oxysporum* and *S. cerevisiae* mixed culture, 20.6 g L^{-1} of bioethanol was produced (productivity 1.0 g L^{-1} h^{-1}) (Prasoulas et al., 2020).

Biodiesel is a liquid biofuel which is conventionally produced from oil crops. However, insufficient availability of feedstocks limits its expansion at a commercial scale. Recently microbe-based biodiesel production has gained immense attention. Numerous oleaginous microorganisms from bacteria, yeast and fungi are known to produce intracellular lipids under specific growth conditions. These microbes can be cultivated on various low-cost feedstocks, including FVW. Ma et al. (2021) reported microbial lipid production by *Lipomyces starkeyi* DSM 70,296 using flour-rich waste (FRW). In the batch and fed-batch modes, the microbial oil contents were 40.4 and 57.8 % (w/w), and the total dry weights were 30.5 and 109.8 g L^{-1}, respectively and productivity of 0.4 g L^{-1} h^{-1} in fed-batch mode. FRW was initially subjected to enzymatic hydrolysis using an enzyme produced by *Aspergillus awamori* through SSF of wheat milling byproducts (Ma et al., 2021). Donzella et al. (2022) used pumpkin food industrial waste for lipid production by *R. azoricus*. With a productivity of 0.26 g L^{-1} h^{-1} and a yield of 0.24 g lipids per g of consumed sugar, the two-stage process resulted in a biomass concentration of 45 g L^{-1} (dry weight) which included 55 % lipids, with a lipid concentration of 24 g L^{-1}.

Biomethane (bio-CH_4) and biochemicals (volatile fatty acids (VFAs)) production using FVW supports proper waste valorization and reduces the dependency on fossil fuels. Zhang et al. (2022) showed that the major hydrolytic bacterium Defluviitoga sp. was enhanced by co-digestion of food waste with kitchen waste (KW) and garden waste (GW), speeding substrate hydrolysis. At an organic loading rate (OLR) of 3 g VS L^{-1} d^{-1}, FW-KW and FW-GW co-digestion increased bio-CH_4 synthesis by 24.69 % and 44.96 %, respectively. As a result, the system could withstand an increase in OLR from 3 to 4 g VS L^{-1} d^{-1}. Mlaik et al.

(2109) studied enzymatic pretreatment of organic fraction of municipal solid waste (OFMSW) for biomethane production and reported higher yield with enzyme-treated OFMSW than raw OFMSW. After pretreatment of OFMSW using WB and OFMSW enzyme cocktails produced from *Aspergillus niger,* the CH_4 potential of OFMSW increased from 189.2 mL gVS^{-1} to 607 and 672 mL gVS^{-1}, respectively. A two-stage (LBR-UASB) integrated AD system's methanogenesis was greatly increased by changing the ratio of substartes (FW and VW). In contrast to the LBR with 2:1 FW:VW (218.54 $mLgVS^{-1}$), which had the greatest methane content of 61 %, the LBR with 2:3 FW: VW had a greater methane output (226.86 $mLgVS^{-1}$ on) with a maximum of 63 % methane content. In contrast to 2:1 FW:VW (340 $gKgVS^{-1}$, 247 $gKgVS^{-1}$, and 340 g $KgVS^{-1}$, respectively), the acetate, propionate, and lactate yields for 2:3 FW: VW were 420 $gKgVS^{-1}$, 87 $gKgVS^{-1}$, and 180 $gKgVS^{-1}$, respectively. The 2:3 FW:VW ratio increased acetate synthesis while decreasing propionate and lactate production, improving the leachate properties in LBR (Chakraborty and Venkata Mohan, 2018).

Biohydrogen (bio-H_2) is a clean fuel that does not generate toxic byproducts upon combustion. Many researchers have studied bio-H_2 production through dark fermentation using FVW. Akca et al. (2021) reported a bio-H_2 yield of 449 mL H_2gVS^{-1} from FW in anaerobic membrane bioreactors. Cappai et al. (2108) reported a maximum H_2 yield of 88.8 L H_2kgVS^{-1} of FW and a maximum production rate of 10.8 L $H_2kgVS{\bullet}h^{-1}$ using an FW to inoculum ratio of 0.14. Sarkar et al. (2020) reported utilising FW under saline environments (40 g NaCl L^{-1}) a maximum H_2 production rate (HPR) of 0.044 L h^{-1} and cumulative H_2 production (CHP) of 1.05 L with a generation of additional butyric acid (C4: 3.04 g L^{-1}), acetic acid (C2: 1.17 g L^{-1}), and traces of valeric acid (C5: 11 mg L^{-1}). Likewise, replacing petrochemical plastics with sustainable alternatives such as biodegradable plastics seems to be a feasible option. Biodegradable plastics are plastic-like substances which may or may not be produced from renewable feedstocks but are biodegradable or compostable. Examples of such plastics include polylactic acid (PLA), polyhydroxyalkanoates (PHA), starch-based and cellulose-based materials. Among these, PHA is a natural biodegradable polymer synthesized entirely through biological routes and has properties similar to conventional plastics (Philip et al., 2007). PHA has been reported to be produced from a variety of food wastes. Chaudhry et al. (2011) reported production of 35.63 % and 20.63 % medium chain length (mcl)-PHA and PHA, respectively, by *Pseudomonas* species grown in corn oil and molasses as carbon sources. 20 % PHA production is reported by activated sludge consortium using tomato wastewater (Liu et al., 2008). Pereira et al. (2021) reported 49.25 % of mcl-PHA, produced by *Pseudomonas chlororaphis* sub sp. *aurantiaca* DSM 19603, grown on apple pulp waste. FVW has also been reported for producing organic acids such as lactic acid, citric acid, acetic acid, propionic acid, butyric acid and succinic acid. Organic acids are produced through SSF or submerged fermentation of various feedstocks. Hakem (2021) reported citric acid production from various fruit wastes. A maximum of 130.50 $mgml^{-1}$ of citric acid was obtained from mango waste, followed by 99.80 $mgmL^{-1}$of grapefruit waste and 40.42 mgmL-1 of banana waste. *Actinobacillus succinogenes* produced 27.03 gL^{-1} of succinic acid from the hydrolysate rich in glucose and fructose, which was produced by hydrolysis of FVW by enzyme cocktail produced by *A. niger* and *R. oryzae* through SSF (Dessie et al., 2018). Enzyme production using FVW is gaining immense attention as it reduces production costs associated with manufacturing and feedstock. Numerous hydrolytic enzymes have been produced by FVW through different fermentation routes. Amylase (728.00 ± 18.20 U/mL) and single cell protein (SCP) have been reported to be produced by *Aspergillus niger* using banana peel medium (Oshoma et al., 2019). Verma and Kumar (2020), reported bottle gourd peel waste, whey, and starch-based hydrolysates as potential carbon sources for cellulase production using *Trichoderma reesei* and *Neurospora crassa*. *Aspergillus flavus* produced xylanase enzyme using passion fruit peel as the sole substrate, which is stable at 55–60 °C and over a broad pH range (Martins et al., 2018). Laccase production from *Bacillus* sp. MSK-01 under SSF conditions using fruit juice waste as the substrate is reported by Sondhi and Saini (2019). Other vegetable wastes such as potato, pumpkin, cauliflower, cabbage and brinjal were studied for protease production using *Aspergillus niger*, where cauliflower and cabbage waste showed maximum enzyme activity of 1.082 U g of the substrate and 0.886 U g of the substrate after 96 h, respectively (Madhumithah et al., 2011). In glucoamylase and protease-rich media, the production of glucoamylase, pectinolytic, lipase, and cellulase enzymes were reported using SSF of kitchen and domestic waste by fungal strains (Abu et al., 2017).

Seed, peels and pomace portion of FVW is a good source of bioactive compounds such as vitamins, short-chain fatty acids, bioethanol, biopolymer, carotenoids, fibres, lignin, polyphenols (phenolic compounds), and non-digestible polysaccharide (cellulose and hemicellulose) can potentially be used in various food and pharmaceutical industries (Dahiya et al. in 2018). Lignin can be found in many food wastes such as wheat straw, peanut husk, peel of citrus fruits and sugarcane baggase, and has been reported to produce a range of bioproducts viz., mixed organic acid, polymers, activated carbon, benzylic aldehyde, and aromatic-rich pyrolysis oil etc. (Ganguly et al., 2020; Wang et al., 2019).

6. Global R&D firms specialized in enzyme production

Enzymes used in industrial applications are generally categorized into technical, food, and feed. The most commonly used technical enzymes are amylases, cellulases, xylanases, proteases, and lipases. Amongst these, amylases and proteases have a massive market due to their versatile applications and available substrates for production. To make the pretreatment process commercially feasible, attempts are made to produce high-titer in-house enzymes with minimum capital investment. The demand for enzymes has increased global competition among leading industrial enzyme producers. Consequently, established companies gradually took over nascent ones to compete with their equivalents more efficiently. DuPont, in 2011 took over a massive stake in Danisco, along with its Genencor division, giving the former a strong lead in the industrial enzyme business, especially in the production of cellulosic ethanol (Kuhad et al., 2011; Althuri et al., 2017).

Industrial enzymes are now widely available, and the key companies are majorly limited to the developed nations such as Denmark, Switzerland, Germany, Netherlands, and USA (See Supplementary Material). Novozymes and Danisco, established in Denmark, provide 70 % of the global demand for industrial enzymes, while Netherland-based Royal D.S.M. serves 6 % of the market (Althuri et al., 2017). In contrast, Japan and China make minor contributions to meet the need for industrial enzymes worldwide. On the other hand, the Indian industries in 2013 occupied a share of $3387.30 million in the global market for enzymes, which is projected to increase further with time by 15 % CAGR (Chandel et al., 2007). Patent rules govern the market value and the regulatory aspects of enzyme application. In this context, Novozymes is leading with the highest number of patents on industrial enzymes compared to other counterparts.

The key players in production and supply of industrial enzymes are Novozymes (Bagsvaerd, Denmark) specialized in technical, food and feed enzymes; D.S.M., (Delft, the Netherlands) known for food and feed enzymes; AB enzymes (Feldberg Strasse, Germany) known for technical, food and feed enzymes; Bio-CAT Microbials (Troy, Shakopee, United States) for probiotics, nutrition, microbiome, and fermentation; Biocatalysts (Chicago, Cardiff) specializes in enzymes, food, synthetic biology and biomanufacturing; Deerland Probiotics & Enzymes (United States and Denmark) provides nutritional supplements, food and beverages; ADM (Illinois, USA) for food and feed enzymes; Grin steel vaeket (Aarthus, Denmark) supply pectinases with trade name pectolase; Amano (Nagoya, Japan) supplies lipases; Biocon Pvt ltd (Bangalore, India) provides several industrial enzymes and Genotex International Private Limited (Hyderabad, Telangana) is renowned for producing

several industrial enzymes (Kumar et al., 2014; Garg et al., 2016) (See Supplementary Material).

7. Applications of hydrolytic enzymes in FVW processing

7.1. Role of exo and endo enzymes during anaerobic digestion of FVW

Microorganisms secrete enzymes that hydrolyze the particulate FVW substrate, converting it into small transportable molecules that can pass the cell membrane. These simple molecules inside the cell provide energy and help to synthesize cellular components. These enzymes convert polysaccharides into simple sugars, as discussed above (Section 4 and Table 2). Xylanase activity during hemicellulolytic degradation and amylase activity during starch hydrolysis yielded identical results where exo enzyme efficiency outside the cell wall was more significant than cell-bound/endo enzyme efficiency (Kosugi et al., 2001). Parawira et al. (2005) explained the enzymatic hydrolysis of potatoes. They saw that for the first 20 days, extracellular protease activity was higher than cell-bound, and an increase followed this in cell-bound enzyme/endo enzyme activity until the hydrolysis phase was over. Exo and endo enzymes, such as exo and endo glucanases and xylanases, synergistically provide better results and boost the absorption of soluble reaction products. The beneficial effects of amylase, galactosidase, and protease were also observed during the co-digestion of FW and sludge (Chakraborty et al., 2018). The hydrolytic phase of AD is highly influenced by enzyme expression and enzymatic activity. However, the activity is coordinated by a group of enzymes simultaneously acting on the substrate. The fluid phase of AD expresses a sophisticated enzyme system consisting of extracellular hydrolases such as lipases, proteases, and glucosidases expressed by cellulolytic bacteria to hydrolyze cellulosic biomass (Menzel et al., 2020). Further, the acidogenic organisms digest the monomers and simultaneously generate short-chain fatty acids and hydrogen as intermediates products of acetogenesis. A syntrophic relationship between acidogenic and acetogenic organisms generates a pool of enzymes that produce organic acids such as acetate and formate. In the absence of oxygen, these organic acids act as the final electron acceptors in the biochemical reactions that generate energy as ATP and other forms, including hydrogen as the intermediate and methane as the final reduced product. In two-stage AD, in which *Clostridium* dominates, butyric-type fermentation is most effective due to the higher production of acetic acid, butyric acid, and hydrogen (Menzel et al., 2020). Additionally, white-rot fungi and other aerobic fungi are frequently used during pretreatment to break down lignocellulosic biomass (FVW) before subjecting them to AD (Shrestha et al., 2017). Table 2 explains the role of endo and exoenzymes in the anaerobic digestion of FVW.

7.2. Enzymatic vs whole-cell bioconversion of FVW

Biotransformation can be achieved by employing whole cells or through cell-free enzymatic systems. Both these bioconversion processes have pros and cons (Bergquist et al., 2020; Claassens et al., 2019). Some critical criteria that determine whether to use enzymes or intact microbial cells for bioconversion are the scale of operation, the requirement for co-factors, and the type of reaction to be carried out. The ready-to-use enzyme readily available in the market can produce a single desired product, which is highly advantageous in process economics. Whereas the use of microbial cells is non-beneficial as microbes, even under controlled conditions, are prone to side metabolic reactions, ending up in more than one product in the reaction medium. Furthermore, unlike isolated enzymes, microbial conversion techniques are limited by a slow reaction rate. This is due to the slow transposition of substrate molecules across the cell membrane towards the enzymes (Bergquist et al., 2020). To address this limitation, microbial cells are often subjected to mild chemical treatments using surfactants, detergents, or solvents or to physical treatment to increase cell permeability. However, these treatment methods can adversely affect the desired product metabolism of the cells apart from cell disruption and other complications during the downstream processing for product recovery (Adrio and Demain, 2014). Besides, the fatty acid composition of microbial cells is another determining factor for cell permeability, enzyme stability, and high activity. Hama et al. (2004) observed that the fatty acid composition of *Rhizopus oryzae* with oleic acid and oleic plus palmitic acids in the ratio of 0.67 was ideal for higher hydrolytic enzyme activity and stability.

On the other hand, enzymatic reactions can be expensive as co-factor regeneration would add to the cost of the enzyme, unlike in the microbial cells that consist of the essential co-factors within them. Also, isolated enzymes' stability is lower than those inside the protected cell environment. Despite these disadvantages, isolated enzymes are still being used owing to the simple experimental set-up and easy operation relative to the microbial bioconversion processes, which suffer from high operation costs, and tedious procedures to obtain the desired end product (Adrio and Demain, 2014; Bergquist et al., 2020). Nevertheless, the commercial utilization of enzymes is influenced primarily by the cost competitiveness of enzymatic systems with the already established chemical/physical/biological treatment methods.

The other advancement in enzyme engineering that is not possible with microbial bioconversion is the feasibility of conducting enzyme catalysis in organic solvents instead of water, as certain enzymes show high activity and stability even in organic media. The organic solvents provide the best conditions for various reactions such as hydroxylation, dehydrogenation of alcohols, polymerization of phenolic compounds, depolymerization of lignin polymer, synthesis of esters, synthesis of peptides and racemic mixtures resolution (Adrio and Demain, 2014). Enzymatic reactions conducted in organic media have the edge over similar reactions conducted in an aqueous medium, which include enhanced non-polar substrate solubility; thermodynamic equilibrium shift towards synthesis than hydrolysis; lesser contamination chances and side reactions; no need for enzyme immobilization because enzymes may be isolated using straightforward filtering methods while being insoluble in organic solvents; low boiling organic medium provides for simple product recovery; small reaction volumes; ability to conduct reactions that are otherwise not possible in an aqueous environment; and the feasibility to use enzymes directly for chemical synthesis (Sanchez and Demain, 2011). The above properties have significantly broadened the applications of industrial enzymes.

Several attempts have been made to apply enzymes for FVW valorization, predominantly as a pretreatment step before microbial treatment to produce platform chemicals and sustainable energy production. In 2016, Haque et al. proposed utilizing bakery wastes to produce biocolourants using *Monascus purpureus*. The processing of kitchen trash by *Bacillus thuringiensis* resulted in bio-pesticides generation in SSF (Zhang et al., 2013). Moon et al. (2009) reported the application of amyloglucosidase and carbohydrase mixture for FW treatment that resulted in 0.46 g/g glucose in 3 h of reaction time, which further on fermentation using *S. cerevisiae* resulted in 0.23 g/g ethanol in 15 h of incubation time. In a separate study, Moon and Song (2011) reported using carbohydrase: protease: lipase in the ratio 1:2:1 for hydrolysis/saccharification of FW (0.2 % w/w) for sugar production. This sugar-rich hydrolysate was then converted to methane (0.35 L-CH_4g-sCOD^{-1}) using an upflow anaerobic sludge blanket (UASB) reactor at an organic loading rate of 9.1 g-sCOD/Ld^{-1}. Sarkar et al. (2016) strategically used acid-shock treated selectively enriched mixed microbiome under alkaline conditions (pH: 10) to obtain enhanced production of VFA from FW. It was reported that VFA of 11.1 g L^{-1} was obtained with a higher acetic acid concentration (6.9 g L^{-1}), butyric acid (2.6 g L^{-1}) and propionic acid (1.3 g L^{-1}) with bio-hydrogen as a byproduct. These studies suggest the effective utilization of FVW using enzymatic followed by whole-cell conversion processes, ensuring low cost waste-to-wealth enterprise.

7.3. Immobilized enzymes and FVW treatment

Industrial use of enzymes is limited mainly due to the high cost and their instability and sensitivity under unfavourable conditions. Moreover, cell-free enzymatic systems catalyze soluble reactions in the aqueous medium; consequently, the recovery and reuse of free enzymes are complex and cost-intensive. Besides, these enzymes may be subjected to feedback inhibition, compromising the enzyme activity for use in the following cycle (Bhat and Sukumaran, 2013). Enzyme immobilization techniques are used to reuse and recycle industrial enzymes, increasing enzyme activity and stability, preventing product contamination with enzyme molecules, and reducing the cost of subsequent enzyme recovery and product purification during the valorization of FVW. These techniques also increase enzyme operability under difficult process conditions (e.g., higher temperatures, adverse pH, etc), resulting in better process stability and a reduction in operating costs (Datta et al., 2013; Zdarta et al., 2021). Enzyme-enzyme cross-linking, carried out on a solid substrate, can avoid structural deformation and improve performance, stability, and half-life in adverse circumstances found in waste streams from the food processing industry. Encapsulation in different polymeric matrices has been shown to resist the local pH around enzymes (cationic and anionic substances shift pH optimum) (Zhang et al., 2016). The acid whey generated during the straining of yoghurt has a pH of 5, which was used for sweetener production using glucose isomerase enzyme, which has pH optima of 7 and 8.5. The lipase enzyme was immobilized to convert fatty acids and alcohols to biodiesel since it is known that alcohols denature lipase (Andler and Goddard, 2018).

Immobilized enzymes have several applications in dairy, food processing, biorefineries, paper and pulp, textile, and detergent industries. Laccases and tyrosinases, manganese, lignin, and phenol peroxidases, in particular, show considerable potential for reducing a variety of phenolic compounds in a specific and highly regulated manner (Zdarta et al., 2021). *Thermomyces lanuginosus* and *Candida antarctica* B immobilized lipases were employed to hydrolyze and esterify lipid splits in rejected/spent oils to produce biodiesel (Bhat and Sukumaran, 2013; Andler and Goddard, 2018). Subsequently, the immobilization of thermophilic enzymes was investigated in the high fructose corn syrup industry and during the valorization of carbohydrate-rich FW streams (Andler and Goddard, 2018). To hydrolyze soy protein isolate for the valorization of protease waste, alcalase alkaline protease from *Bacillus licheniformis* was immobilized on magnetic nanoparticles coated in chitosan (Yu et al., 2013). Starch-rich waste produced from food processing industries can be effectively treated in a circular economy with immobilized amylase and converted to glucose, which is the building block of several other sustainable chemicals (Fig. 3).

7.4. Nano-enzymes in FVW processing

Nanotechnology allows novel strategies for enzyme immobilization by stabilizing enzymes on nanostructures, including nanoparticles, nanofibers, and nanorods. The activity of enzymes immobilized in nanostructures increases due to the reduced enzyme-enzyme and denaturing interactions between the enzyme and the solid support (Verma et al., 2013). For macromolecular systems suffering from mass transfer limitations, using nano-enzymes is a possible solution to increase the product yield. The nanoparticle-bound enzyme in an aqueous solution exhibit the property of Brownian movement, thereby increasing its activity compared to free enzymatic systems. In general, linking enzymes to nanoparticle matrix limits the unfolding of proteins and improves the stability and performance of bound enzymes (Gupta et al., 2011). The nano-matrix may be made from cellulose, chitosan, polyhydroxybutyrate, silica, gold and silver, polystyrene, and titanium dioxide nanoparticles. Amongst others, magnetic nanoparticle-bound enzymes are advantageous as these can be easily separated under an external magnetic field.

In contrast, polymeric nanoparticles made from naturally occurring biopolymers such as cellulose and chitosan are considered biodegradable, biocompatible, and eco-friendly nanoparticles (Seenuvasan et al., 2018; Basavegowda and Baek, 2021). Enzymes may be conjugated to

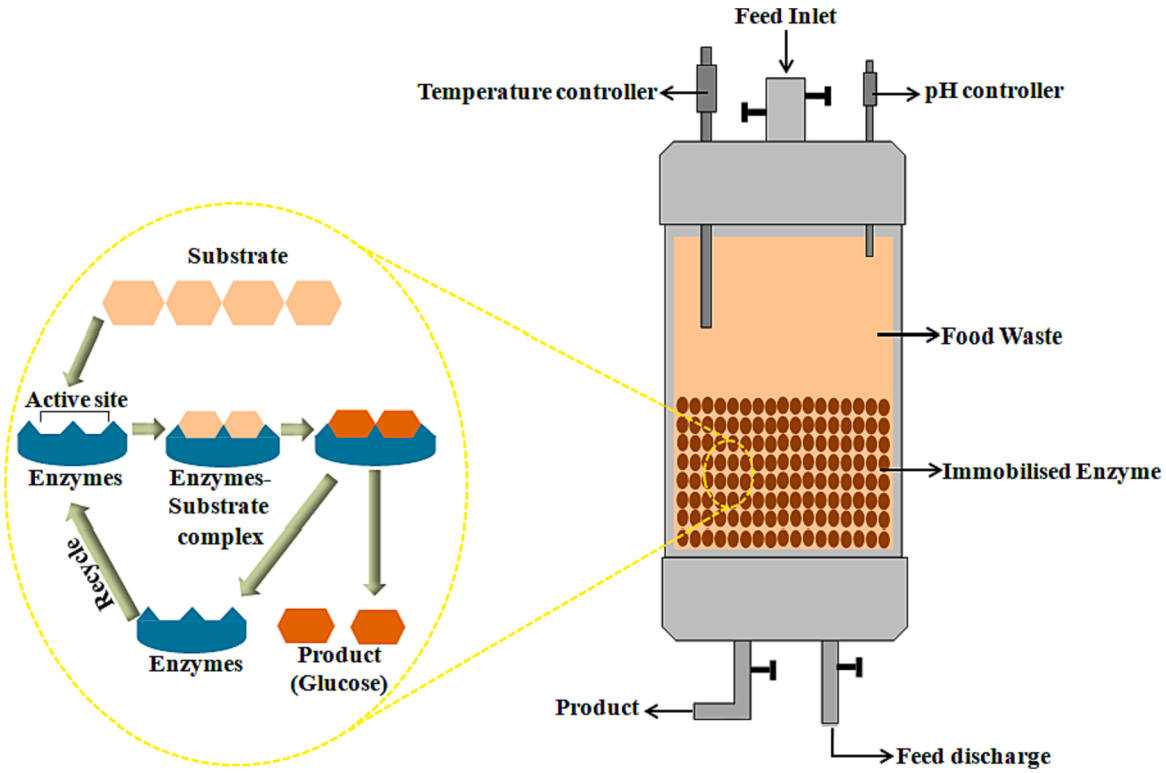

Fig. 3. Immobilized enzymatic system for food and vegetable waste treatment.

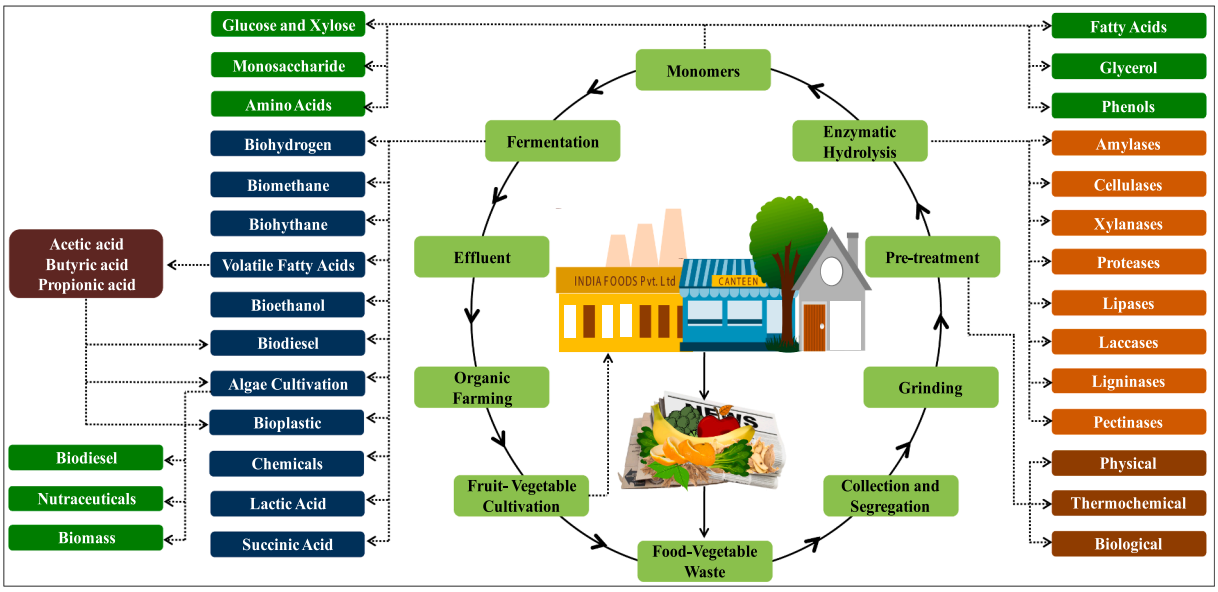

Fig. 4. Role of enzymes in the valorization of food and vegetable waste in the circular economy framework.

nanoparticles through electrostatic adsorption, covalent binding, affinity binding, or direct reaction with the chemical groups on the protein surface. Electrostatic adsorption is the most commonly used method where interactions between enzymes and nanoparticles can be controlled by the pH of the reaction medium (Seenuvasan et al., 2018). Covalent binding is a reliable method for enzyme immobilization onto nanoparticles where the surface chemistry of nanoparticles can be controlled through functional group modifications. For instance, metal oxide nanoparticles can be surface functionalized through silanization resulting in the exposure of amino groups that can act as linking sites for several enzymatic systems. In affinity binding, the specific binding property of a particular enzyme type is exploited, and the nanoparticle surface is modified accordingly to enable affinity adsorption. One notable example is the use of streptavidin to coat nanoparticle surfaces to specifically bind biotin-labelled enzymes (Seenuvasan et al., 2018; Basavegowda and Baek, 2021). Direct conjugation of gold (Au), silver (Ag), or sulfur-containing nanoparticles (ZnS/CdSe) is possible via thiol (Au-S and Ag-S) or disulfide binding of cysteine in the enzymes (Ahmad and Sardar, 2015). Lipase from *Subtilisin carlsberg* and *Candida antarctica* was physically adsorbed onto fumed silica nanoparticles to transesterify *N*-acetyl-l-phenylalanine ethyl ester and (RS)-1-phenyl ethanol in hexane, resulting in higher enzyme stability and catalytic activity compared to non-immobilized commercial enzymes (Cruz et al., 2011). In a separate study, starch degradation was conducted using α-amylase immobilized poly [2-hydroxyethyl methacrylate-*N*-methacryloyl-(L)-phenylalanine] magnetic nanoparticles, which resulted in high loading of 705 mg of enzyme/g nanoparticles wherein 85 % of specific activity could be retained even after ten cycles of reuse (Uygun et al. 2012). Ahmad and Sardar (2015), in another study, reported higher temperature stability and activity of industrial enzymes, viz., cellulase and α-amylase, upon immobilization on titanium dioxide (TiO_2) nanoparticles compared to their free enzymatic equivalents (Ahmad and Sardar, 2015). β-Glucosidase from *Aspergillus niger* covalently linked to functionalized iron oxide nanoparticles was used for biofuel production. It was observed that enzyme-immobilized nanoparticles could retain 50 % of their initial activity until the 16th cycle of reuse and showed higher temperature stability (70 °C) than soluble enzyme counterparts (Verma et al., 2013). These studies demonstrate nano-biocatalysts' value by influencing the enzymes' catalytic activity. Nanoparticles' high surface area, high enzyme loading, high enzyme availability, and high mass transfer resistance make them the ideal matrix for nano-biocatalysts in organic waste treatment (Van Pelt et al., 2018). Materials such as PbO, Mo, Ni, Co, Ag and SiO_2 can be recovered from the effluent and sludge of food-processing industrial wastewater treatment. A circular economy approach can be followed to extract value-added products from FVW while concurrently treating sludge. First, the metals can be extracted for nanoparticle synthesis, and the nanoparticles are used to immobilize the enzymes involved in FVW valorization.

8. FVW valorization in the circular economy

The "greening" of chemical production is the century's most urgent socioeconomic and technological need. It might be accomplished by continuing the transition to a bio-based economy using renewable biomass as the raw material resource. The rising demand for energy and resources is compelling humanity to switch from a fossil-based linear economy to a sustainable circular bioeconomy (Venkata Mohan et al., 2020). Enzyme-based biomass conversion is crucial for advancing a sustainable circular economy that uses renewable raw materials instead of fossil fuels. The value-added use of FVW as a feedstock is still a desirable option that works well with the circular economy strategy. Fermentable sugars derived from FVW hydrolysis could be converted into biofuels (biohydrogen, biomethane, biodiesel), platform chemicals (simple sugars, fatty acids, bioethanol, biopolymers), bioelectricity, biofertilizers, animal feed, and other value-added products in a bio-based economy, using clean, enzymatic processes in an integrated biorefinery as depicted in Fig. 4 (Venkata Mohan et al., 2016). Biorefineries are incredibly energy-efficient, facilitating zero-waste production and allowing companies to produce environmentally beneficial products sustainably. Biorefineries enable the concept of a circular economy where biodegradable materials are used, and bioproducts can be manufactured so they can get back to nature without causing damage to the environment at the end of their useful life (Fig. 4). The circular bioeconomy is a resource utilization system with the fundamental principles of reducing, reusing, and recycling. A circular, waste-based, sustainable bioeconomy might be developed as a result of the integrated biorefinery of FVW and could give tough competition to fossil-based refineries and address numerous environmental issues (Dahiya et al., 2018; Venkata Mohan et al., 2016). In the study by Chakraborty and Venkata Mohan (2019), FVW was treated through a three-stage integrated process. FW and vegetable waste were co-digested in LBR for hydrolysis and acidogenesis. Followed by an airlift reactor (ALR) for methanogenesis, and finally, untreated FVW from the first and second stages was composted to make a resource-efficient and zero-discharge

biorefinery model. Off gas from LBR was diverted to ALR to enhance methane recovery. The food industry releases enormous amounts of lignocellulosic FVW every year, which has the potential to be used as a renewable aromatic feedstock. It might be utilized as a substitute for benzene, toluene, and xylenes (BTX) obtained from fossil resources. The process of valuing lignin involves reductive catalytic fractionation (RCF), which produces highly depolymerized lignin oil with a small number of aromatic monomers and possible platform chemicals (Sun et al., 2018). As an alternative to reductive catalytic fractionation, lignin can be transformed using fermentation into common compounds such as cis, *cis*-muconic acid, platform chemicals for manufacturing polyesters, polyamides, and polyurethanes, as well as terephthalic acid via isomerization (Sheldon, 2020). Lignocellulosic waste is a rich source of low-cost carbohydrates which can take the place of traditional carbon sources as the raw materials for various high-value goods, including bioethanol, organic acids, enzymes, and biodegradable plastics (Ravindran and Jaiswal, 2016). Similarly, pectinase and cellulase-based clarification technologies for the canning industry were developed, and these enzymes can be recovered from FVW generated in the same industry via SSF. Furthermore, ethanol can be produced from lignocellulosic FVW rich in starch using amylase, cellulase, and hemicellulase, lowering the raw material input cost. Fungal enzymes, such as pectinases, glucanases, and hemicellulases, are used in wine production and can be produced through the SSF of FVW. These freshly formed enzymes enhance colour extraction, skin maceration, must clarity, filtration, and wine quality and stability. *Bacillus subtilis* produced cellulase and amylase using high lignocellulosic content banana trash as a feedstock (Kuhad et al., 2011).

8.1. Role of cross-linked enzyme aggregates in FVW valorization

The carrier-free method of immobilizing an enzyme cocktail in the form of cross-linked enzyme aggregates (CLEA) is highly stable against leaching in aqueous conditions. It possesses operational stability, making it suitable for usage in a circular economy (Van Pelt et al., 2018). CLEA of cellulolytic and hemicellulolytic enzymes can biotransform cellulose and hemicellulose into fermentable sugars by catalyzing oxidative backbone cleavage to its constituent sugars, primarily xylose and mannose, and functional group removal of polysaccharides with the aid of ancillary enzymes (Bornscheuer et al., 2014; Sheldon, 2020). These enzyme complexes are found in the *in vivo* cellulosomes and are generated by several cellulolytic fungi and bacteria. They can be immobilized as combi-CLEAs, making them excellent candidates for the application of cost-effective lignocellulolytic enzymes and process optimization to lower pretreatment costs and the total price of second generation (2G) bioethanol. For instance, pre-treated sugarcane bagasse and milled corn stover were successfully converted using a xylanase-mannanase combi-CLEA. The ammonia-cooked sugarcane bagasse was successfully hydrolyzed by the combi-CLEA and recycled six times (Bhattacharya and Pletschke, 2015). Waste from the food industry may be recycled and utilized as the initial raw material for producing enzyme cocktails using SSF and several other sustainable biochemical and fuel productions to improve the process's economics and enable self-sustainability. This circular approach can replace the feasibility of precious metal catalysts for commercial use by resulting in multiple product generations and positively influencing the overall techno-economic aspects of the bioprocess (Fig. 4). Future developments in metagenomics, enzyme-directed evolution, and metabolic pathway engineering of complete microbial cells, supported by bioinformatics improvements, allow the development of enzymatic processes that are more specific and economically viable.

9. Importance of life cycle assessment for the enzymatic valorization of FVW.

The current discussion explores the importance of life-cycle (LCA) and techno-economic assessment (TEA) as decision-making tools for selecting the most environment-friendly, mature and instructional technologies. FVW valorization system to generate value-added products. The two main categories of LCA techniques are attributional and consequential. The former is intended to give a consistent image of the average circumstances while excluding the influences of the market. In contrast, the latter quantifies the implications of the change made to the system. The generation of CO_2 (implying the possibility of global warming), the patterns of water and land use, and numerous other elements all have a significant role in determining the environmental effects of FVW. However, few available reports on the environmental performance of the industrial-scale FVW valorization, LCA and energy balance of the lab- and pilot-scale waste refineries for the enzymatic treatment of FVW are discussed in this section. Murphy and Kendall, (2015) performed a life cycle analysis of biochemical cellulosic ethanol under multiple scenarios where life cycle inventory (LCI) data for material and energy inputs were derived from LCI databases such as Ecoinvent and GaBi Professional. The environmental impacts of water solvents, organic co-solvents, metal catalysts, reaction temperature, and time were evaluated, and enzymatic biofuel technology was compared to other traditional methods in a LCA to assess the environmental effects of pre-combustion activities, feedstock production, conversion facility operations, etc. Murphy and Kendall (2015) reported that cellulosic ethanol could significantly reduce greenhouse gas (GHG) emissions in comparison to conventional transportation fuels (45–60 g CO_2/MJ), though substantial uncertainty exists. The environmental consequences of using FVW to produce biogas using AD were investigated by Woon et al. (2016). Likewise, Karka et al. (2017) conducted an extensive LCA study to examine the environmental impacts of producing 23 products, including diverse chemicals, biodiesel, and biogas, utilizing five different types of biomass waste (wood chips, municipal solid waste, rapeseed oil, wheat straw, and waste cooking oil). One report on bread waste conversion into hydroxyl methyl furfural (HMF) suggested that employing a water–acetone medium and the non-toxic aluminium chloride ($AlCl_3$) catalyst has a positive environmental impact (Lam et al., 2018). Using LCA, the recovery of metals and energy from waste using an enzymatic process was previously compared with incineration from the perspectives of both energy and the environment. Results depicted that the metals and energy recovery improved more in the enzymatic process than in incineration (Jensen et al. 2010).

Integrating FVW into biorefinery will support the bioeconomy with microbial processes by producing value-added products such as organic acids, enzymes, single-cell proteins, ethanol, and biopolymers (Lakshmi et al., 2021). The 4R framework (reduce, reuse, recycle and recover) in waste management with a circular bioeconomy may be used to value FW by recovering nutrients and producing energy/metabolites from it by integrating to myco-biorefinery (Fig. 4) (Yu et al., 2021). Recently, the extraction of liquid and solid biofertilizers from FW has been speeding up using fungal (*Aspergillus*) hydrolytic enzymes (Ma et al., 2020). The development of efficient, reliable enzymes and the enhancement of the fermentation process were carried out by applying 3R strategy to overcome the barriers to bioethanol production (Yan et al., 2020). Their expensive production costs can constrain the use of enzymes in the industry. The SSF of enzyme-producing bacteria outlined in Section 4 could be a prelude to this process by using affordable carbon, nitrogen, and energy sources, including FVW. Compared to submerged fermentation, the SSF method uses less water, energy, and sludge to produce enzymes (Chilakamarry et al., 2022). Filamentous fungi synthesize organic acids, enzymes, phenolic antioxidants, bioethanol, food, and medicinal products (Tuly et al., 2022). However, different operating conditions, particular substrates, and downstream processing are required to manufacture each commercial enzyme and should be optimized for more enzyme output. FW are superior to agricultural residues because they contain a larger amount of dietary supplements; as a result, no additional nutritional supplements are needed to be added during the enzyme synthesis process (Uçkun Kran et al., 2015).

10. Conclusion and future prospective

The current review demonstrates the potential of enzymatic treatment methods for FVW valorization to produce commercially relevant platform chemicals and value-added products, thereby contributing to the ongoing transition from conventional fossil-based energy to renewable and more affordable bioenergy. This review reveals how advances in enzyme treatment and its mechanism in FVW management have a competitive advantage over traditional FVW management practices. The industrial production, environmental and economic impacts, and LCA of enzymatic treatment were discussed. Furthermore, this review demonstrates the opportunity to create a circular economy through the enzymatic treatment of FVW.

Availability of data and material: All data generated or analyzed during this study are included in this published article and its supplementary information files.

CRediT authorship contribution statement

Debkumar Chakraborty: Conceptualization, Visualization, Validation, Writing – original draft, Writing – review & editing. **Sulogna Chatterjee:** Conceptualization. **Avanthi Althuri:** Conceptualization, Writing – original draft. **Sankar Ganesh Palani:** Writing – review & editing. **S. Venkata Mohan:** Resources, Funding acquisition, Supervision, Project administration, Writing – review & editing.

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

No data was used for the research described in the article.

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Appendix A. Supplementary data

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