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Engineering and application of polysaccharides and proteins-based nanobiocatalysts in the recovery of toxic metals, phosphorous, and ammonia from wastewater: A review

Masoumeh Ghalkhani^{a,*}, Hakimeh Teymourinia^c, Fatemeh Ebrahimi^b, Neda Irannejad^d, Hassan Karimi-Maleh^{e,**}, Ceren Karaman^{f,g}, Fatemeh Karimi^a, Elena Niculina Dragoi^h, Eric Lichtfouse^{i,*}, Jagpreet Singh^j

^a Electrochemical Sensors Research Laboratory, Department of Chemistry, Faculty of Science, Shahid Rajaei Teacher Training University, Tehran, Iran

^b Thin Layer and Nanotechnology Laboratory, Department of Chemical Technologies, Iranian Research Organization for Science and Technology (IROST), Tehran, Iran

^c Department of Chemistry, University of Zanjan, Zanjan, Iran

^d Department of Chemistry, Isfahan University of Technology, Isfahan, Iran

^e School of Resources and Environment, University of Electronic Science and Technology of China, 611731, Xiyuan Ave, Chengdu, PR China

^f Department of Electricity and Energy, Vocational School of Technical Sciences, Akdeniz University, Antalya 07070, Turkey

^g School of Engineering, Lebanese American University, Byblos, Lebanon

^h "Cristofor Simionescu" Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University, Bld. D. Mangeron no 73, 700050, Iasi, Romania

ⁱ State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, PR China

^j Department of Chemistry, University Centre for Research & Development, Chandigarh University, Mohali-140413, Punjab, India

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ABSTRACT

Global waste production is anticipated reach to 2.59 billion tons in 2030, thus accentuating issues of environmental pollution and health security. 37 % of waste is landfilled, 33 % is discharged or burned in open areas, and only 13.5 % is recycled, which makes waste management poorly efficient in the context of the circular economy. There is, therefore, a need for methods to recycle waste into valuable materials through the resource recovery process. Progress in the field of recycling is strongly dependent on the development of efficient, stable, and reusable yet inexpensive catalysts. In this case, growing attention has been paid to the development and application of nanobiocatalysts with promising features. The main purpose of this review paper is to: (i) introduce nanobiomaterials and describe their effective role in the preparation of functional nanobiocatalysts for the resource recovery aims; (ii) provide production methods and the efficiency improvement of nanobiocatalysts; (iii) give a comprehensive description of valued resource recovery for reducing toxic chemicals from the contaminated environment; (iv) describe various technologies for the valued resource recovery; (v) state the limitation of the valued resource recovery; (vi) and finally economic importance and current scenario of nanobiocatalysts strategies applicable for the resource recovery processes.

1. Introduction

One of the serious problems of the present age is the massive and unfortunately growing amount of waste generation and its disposal. Global waste production is anticipated reach to 2.59 billion tons in 2030, thus accentuating issues of environmental pollution and health

security [1]. Unfortunately, not all begotten waste is gathered. Estimates show that developed countries collect about 96 % of waste, compared to <40 % in poor countries. 37 % of waste is landfilled, 33 % is discharged or burned in open areas, and only 13.5 % is recycled, which makes waste management poorly efficient in the context of the circular economy [2].

There are four general operations for municipal waste treatment:

* Corresponding authors.

** Correspondence to: H. Karimi-Maleh, School of Resources and Environment, University of Electronic Science and Technology of China, 611731, Xiyuan Ave, Chengdu, PR China.

E-mail addresses: ghalkhani@sru.ac.ir (M. Ghalkhani), hassan@uestc.edu.cn (H. Karimi-Maleh), eric.lichtfouse@gmail.com (E. Lichtfouse).

landfilling, recycling, incineration (with and without energy recovery), and composting and digestion [3]. About 45 % of municipal solid waste is composed of organic compounds that contain important elements such as nitrogen and phosphorus [4]. Municipal solid waste treatment is mainly done by anaerobic digestion, which leads to the production of sludge-like material. Unfortunately, in the costly digestion process, not only nutrients and useful wastes cannot be extracted, but also requires further treatment steps such as composting before disposing of in designated areas. The sludge from the digestion process contains different contaminants that make dangerous and risky its use in agriculture. Even though agricultural waste has been used in the past to feed livestock, the probable animal intolerance and health risks prevent this type of use without proper pre-treatment. Moreover, due to the potential effects of waste compounds such as polyphenols on the germination and growth of plants, the composting process is not a problem-free option [5].

Typical waste management approaches focus on the elimination of pollution sources and greenhouse gas emissions that have not yet yielded satisfactory results. An integrated waste management strategy with waste recycling and resource recovery can be a more effective solution. One of the major problems right now is the sustainable management of the huge amounts of waste generated, which must be done efficiently to avoid damaging the environment and creating environmental consequences in the future. The vision of effective and sustainable waste management is the development of technologies in line with the concept of “trash to cash” with the production and replacement of renewable materials, fuels and chemical compounds in industries. The international community is moving toward the use of renewable biological resources and the production of recoverable bio-based products [6]. Economic sustainability, significant waste consumption, great product efficiency, biocompatibility, and residual waste handling should be considered in the production process and waste management. There is therefore a need for methods to recycle waste into valuable materials. By managing different waste sources and applying sustainable development strategies, it is possible to maintain a balance between the economy, society and the environment, and to promote the integration of technology and industry with the sustainability and preservation of environmental health.

In 2016, Rostro-Alanis et al. reviewed the diverse developed nanocarriers for nanobiocatalysts production with emphasis on polymers-based carriers [7]. They described the application of nanobiocatalysts in bioconversion systems, bioelectronics, and proteomic investigation. In 2015, Misson et al. reviewed the developed nanocarriers and applied strategies for enzyme stabilization [8]. They illustrated that immobilizing enzyme by nanocarriers or nanocontainers leads to the enhancement of the catalytic performance and the stability of enzymes. They indicated that proper conformation change upon immobilizing enzymes in nanobiocatalysts structures plays an effective role on their catalytic performance enhancement because provides a more facile interaction of the active site of the enzyme with the target analyte. Moreover, the usage of magnetic nanomaterials in nanobiocatalysts structures facilitates their recovery and reutilization, which causes effective economic savings. In a chapter book published in 2022, Balan Et al. reviewed the diverse immobilization methods developed for enzymes and the application of prepared enzyme-based nanobiocatalysts for bioconversion [9]. However, a comprehensive review paper focusing on engineering and application of polysaccharides and proteins-based nanobiocatalysts in resource recovery from wastewater has not been published.

In the present review, nanobiocatalysts are introduced along with a comprehensive description of biomaterials resources used for their preparation. The nanomaterials employed for fabrication of nanobiocatalysts including metal-organic frameworks, metal oxides, magnetic compounds, and inorganic nanoscaffolds are reviewed. The production methods of nanobiocatalysts and technologies for resource recovery based on nanobiocatalysts are discussed. The advantages and limitation of application of nanobiocatalysts for valued resource

recovery are illustrated. Finally, economical aspects of the use of various biological macromolecules including polysaccharides and proteins for resource recovery are highlighted. In collecting required information and data for writing the present review, the focus was on the nanobiocatalyst word, resource recovery statement of toxic metals, phosphorus, and ammonia.

2. Types of nanobiocatalysts

Nanotechnology is an interdisciplinary field based on structures with 1.0 nm to several hundred nanometers dimensions, which has led to an explosive revolution in research activities [10,11]. Thanks to the recent advances in nanomaterial science, state-of-art advances in catalyst engineering [12,13], energy [14,15], biotechnology and biomedical applications [16–21], genetic engineering [22], mechanical and petroleum engineering [23], optics and electronics [24], food safety, hydrogen production and storage [25–27], and environmental applications [28–31], sensors [32–34], etc. have been accelerated substantially. Among developed nanostructures with unique properties and exceptional performance, nanobiomaterials have received much attention due to the synergistic role of their extraordinary small size and biological properties [35]. Biomaterials are defined as following statements [36–38]:

- (I) Natural materials synthesized from a biomolecule or conventional substance, which are encapsulated or immobilized using a biomolecule that can enhance or replace a biological part of the body such as tissue, organ, or specific function.
- (II) Synthetic structures fabricated from one material or a combination of several materials, such as metals, polymers, alloys, and ceramics, which can replace part of a living organ or operate in contact with living tissues.

Nanobiomaterials are nanostructures composed either wholly or partially of biological molecules such as proteins, nucleic acids, enzymes, poly/oligosaccharides, and antibodies. Biological resources are known as one of the primary sources for the synthesis of nanobiomaterials [38]:

> Plant extracts

The extracted active chemical compounds by removing plant tissue are generally known as plant extracts. These compounds have become viable due to their availability, abundance, and eco-friendly qualities. Plant functional groups, proteins and amino acids, polysaccharides, ketones, and carbonyls, play a reductive role in the environment. Therefore, plant extracts are the perfect option for reducing metal ions in facilitating the biosynthetic process of metal nanostructures [39].

> Microbes

Microbes, bacteria, fungi, microalgae, and in general, microorganisms are a perfect choice for the biosynthesis of nanostructures. This method has attracted much attention due to achieving the desired morphology, size, chemical composition, ease of maintenance, cultivation and scale-up of cells, scale control, and excellent adaptation to various environmental conditions [40].

> Virus

Viruses, as natural nanoparticles with a diameter of 20 to 500 nm, in the role of non-cellular parasites, can infect their host cells by transmitting their genetic material, double-stranded or single-stranded fragments. Animals, bacteria, and plants can act as host cells for viruses. Depending on the host cell type, viruses fall into three general categories: mycophages, bacteriophages, and phytophages [41]. Meanwhile,

phytophages (plant viruses) are a unique biomaterial synthesis platform. The inability of phytophages in human contamination, ease of design, no need for an envelope, the ability to control the size and formation of various morphologies (helix: rigid rod, quasi-spherical: icosahedral), stability under harsh environmental conditions make these structures a good choice for the synthesis of nanobiomaterials [42,43].

> Polysaccharides

Carbohydrates are one of the most abundant biomolecules known in nature. These structures are found in various forms, mono-, oligo-, and polysaccharides. Algae, plants, and wood are significant sources of polysaccharides. High biocompatibility and good biodegradability are some of the fantastic features of these structures. Cellulose and starch as derivative polysaccharides, with ease of processing, abundance, and high tensile strength, have attracted much attention [44,45].

> Proteins

Proteins are defined as vital parts of biological systems. In addition to animal sources, creatine, collagen, elastin, and silk are plant sources of protein structures. These structures are used as biological patterns to synthesize nanostructures. Synthesized nanofibers and nanoparticles are used in many medical, textile, and chemical applications [46,47].

In the dimensions of nanostructures, the created quantum effects play an influential role in determining their optical, chemical, electrical, and magnetic properties [48,49]. The features of grain boundary sliding and short-range diffusion healing have improved nanobiomaterials strength and flexibility. Biological sources-based nanomaterials have better mechanical stability and adhesion than other nanostructures [50,51]. Due to their unique physical, chemical, electrical, and biological properties, nanobiomaterials have found a variety of applications in medicine [52], catalysts and photocatalysts [53–55], and agriculture [56].

The nature of the structural atomic bonds determines the chemical properties of nanobiomaterials. Unsaturated atoms on the surface have higher surface energy and reactivity than saturated ones. The presence of incomplete bonds on the nanobiomaterials surface facilitates their interaction with other nanomaterials or nanocomposites. Solubility as an essential determinant of performance is influenced by the source of nanobiomaterials' synthesis. The presence of hydroxyl functional groups increases aquatic solubility due to the possibility of forming strong hydrogen bonds with water molecules. Bioreactivity, biocompatibility, and biodegradability are prominent features of nanobiomaterials [38]. Nanobiomaterials have a variety of applications in different areas:

Tissue engineering is one of the most comprehensive nanobiomaterials applications. Tissue engineering is a multidisciplinary field in surgical and therapeutic methods to regenerate defected and damaged tissues and restore their general or partial function. This technology uses a scaffold capable of carrying biologically active molecules. The advent of nanobiostructures with the ability to connect and interact directly with tissue surface receptors and the possibility of design in various structures of nano-particles, -fibers, -tubes, -and films have created a dramatic change in tissue regeneration [57,58].

Nanomedicine reduces the dose of the drugs and subsequently minimizes the side effects, improving targeting and the possibility of controlling site-specific drug release. Nanobiostructures, with their very high specific surface area and unique characteristics, have made possible the achievement of these goals [59,60].

Drug delivery accounts as one of the most widely used applications of nanobiostructures. These structures have high potential in designing drug delivery systems with appropriate pharmacological effects, the possibility of controlling solubility in different environments, successful and controlled drug release, increasing drug delivery rate, and having minor side effects [61,62].

Nanobiosensor consists of a nanobiological-based probe to identify an analyte, biomolecule, or combination of various biological elements and a transducer to convert electrical, physicochemical, electrochemical, optical, or thermal signals. Nano bioelectrochemical sensors, with their very high specific surface area, electrocatalytic activity, unique electronic properties, and excellent biocompatibility, have created a massive revolution in acquiring super-sensitive biosensors [63,64].

Bio-imaging is a molecular imaging method to study biochemical and molecular changes during the disease process. Nanobiomaterials are a perfect choice to improve the performance of molecular imaging. These structures, with the possibility of controlled and selective binding to the receptor of the desired biological molecule, very high specific surface area, and environmental compatibility, have a special place in molecular imaging methods such as ultrasound, computed tomography, and magnetic resonance imaging [51].

Nanobiocatalyst has created new horizons for highly efficient catalysts in large-scale industrial applications. In nanobiocatalysts, the high surface-to-volume ratio and the ability of the structure to bind or be exposed to biomolecules reduce diffuse limitations, leading to the achievement of very high catalytic activity [65].

The encounter between biotechnology and nanotechnology led to the emergence of innovative ideas and the introduction of nanobiocatalysts, which could significantly enhance catalytic activity by constraining biomolecules at the nanoscale and at the least conformational cost [65]. A nanobiocatalyst is formed by biomolecule stabilization in the presence of nanostructured carriers. The company of nanocarriers with specific functional groups allows biomolecules to act as information storage and processing systems in ordered nanoscale structures. Nanobiocatalysts promise a more stable designed system that achieves maximum efficiency by providing a huge surface area for loading biomolecules and reducing mass transfer resistance [66]. The advantages of nanobiocatalysts are summarized in the synergistic role of their nano- and bio-structures [8,67]. The cost effectiveness, biodegradability, recyclability, huge surface area, regio- and stereoselectivity, high catalytic activity, and working under mild conditions with low energy consumption and producing less byproduct are the main benefits of nanobiocatalysts. Meanwhile, they encounter some drawbacks such as nanotoxicity which is dangerous for humans and the environment and inactivation at high temperatures, alkaline conditions, and in polar organic solvents.

The main constituents of nanobiocatalysts used in transesterification processes are nanoparticles and biological components. Nanobiocatalysts can be classified according to the type of nanoparticles or the enzyme immobilization strategy. Metal-organic frameworks, metal oxide nanoparticles, magnetic nanoparticles, also carbon-based and inorganic nanostructures are five crucial classes of nanoparticles employed in the development of nanobiocatalysts utilized in energy production through transesterification for resource recovery. **Table 1** describes research on resource recovery through biodiesel production from diverse natural oils using nanobiocatalysts. Here, the nanomaterials and biomaterial used for nanobiocatalyst synthesis, feedstock and experimental conditions for biodiesel production, and the method of enzyme recovery are briefly described. In general, the process of biodiesel production using nanobiocatalysts is similar to the methodology used in the presence of simple nanocatalysts. These steps involve combining specific amounts of water, alcohol, and feedstock such as biomass, vegetable oils, edible oils, and nanobiocatalysts in the reaction conical flask. The mixture is stirred for a particular time at a specific temperature. The resulting products, including biodiesel mixture and glycerol, are separated and purified in a rotary evaporator. The remaining nanobiocatalysts are separated by centrifugation or magnetic field application, depending on their nature [68,69].

Table 1

Nanobiocatalysts developed for biodiesel production as resource recovery. The nanomaterials and biomaterial used for nanobiocatalyst synthesis, feedstock and conditions for biodiesel production, and the method of enzyme recovery are described.

Nanomaterial	Biomaterial	Feedstock	Yield	Time/ temperature	Retaining activity after	Enzyme recovery by	References
GA-Fe ₃ O ₄	<i>Candida rugose</i> lipase	Waste cooking oil	93.58 %	1.5 h/40 °C	3 runs	–	[74]
GA-AP-Fe ₃ O ₄	<i>Rhizopus oryzae</i> lipase	<i>Chlorella vulgaris</i> micro algae bio-oil	69.8 wt %	24 h/45 °C	–	–	[75]
AP-Fe ₃ O ₄	CLEAS of <i>Candida Antarctica</i> lipase B	Waste cooking oil	71 %	36 h/35 °C	6 runs	–	[76]
GA-AP-Fe ₃ O ₄	<i>Candida antarctica</i> lipase	Rapeseed oil	89.4 %	24 h/45 °C	≥70 %, 5 runs	Magnetic field	[77]
AP-GO-Fe ₃ O ₄	–	Non-edible <i>R. communis</i> oil	78 %	48 h	5 runs	Magnetic field	[78]
PDA-Fe ₃ O ₄	<i>Aspergillus terreus</i> AH-F ₂ lipase	Waste cooking oil	92 %	30 h/37 °C	4 runs	Magnetic field	[79]
P(GMA-coMAA)-Fe ₃ O ₄	<i>Candida rugosa</i> lipase	Soybean oil	92.8 %	40 °C	79.4 %, 5 runs	Magnetic field	[80]
Fe ₃ O ₄ @PDA	<i>Pseudomonas cepacia</i> lipase	Soybean oil	90 %	12 h/37 °C	3 run _≥	Magnetic field	[81]
GA-Fe ₃ O ₄	<i>Candida antarctica</i> lipase B	<i>Chlorella vulgaris</i> lipids	≥90 %	3 h/30 °C	90 %, 10 runs	Magnetic field	[82]
CeO ₂ nanorods/ PDA	<i>A. terreus</i> Lipase	Non-edible <i>Eruca sativa</i> Seed oil	89.3 %	30 h/35 °C	5 runs	Centrifugation	[83]
PEI-Fe ₃ O ₄ cluster@SiO ₂	<i>Pseudomonas cepacia</i> lipase	Palm oil	88.9 %	24 h/50 °C	~65 %, 5 runs	Magnetic field	[84]
MGO-Fe ₃ O ₄ -AP- GA	<i>Rhizopus oryzae</i> lipase	<i>Chlorella vulgaris</i> bio-oil	~70 %	24 h/45 °C	58.8 %, 5 runs	Magnetic field	[85]
mCNTs-Fe ₃ O ₄ - PAMAM	<i>Burkholderia cepacia</i> lipase	Soybean oil	92.8 %	35 °C	90 %, 20 runs	Magnetic field	[86]
Fe ₃ O ₄ @SiO ₂ -AP- GA	Lipase NS81006 of the <i>Aspergillus niger</i>	–	71 %	12 h/45 °C	5 runs	Strong Magnetic field	[87]
Fe ₃ O ₄ NPs-GO	<i>Candida rugose</i> lipase	Soybean oil	92.8 %	60 h/40 °C	75.8 %, 5 runs	Magnetic field	[88]
ZIF-8	<i>Rhizomucor miehei</i> lipase	Soybean oil	95.6 %	24 h/45 °C	84.7 %, 10 runs	–	[89]
Cu-MOF	Porcine pancreas lipase	Sunflower oil	96.5 %	45 °C	72.5 %, 5 runs	–	[90]
Co-MOF	<i>Candida rugose</i> lipase	Soybean oil	78.5 %	60 h/45 °C	56.0 %, 6 runs	Centrifugation (6000 rpm, 5 min)	[71]
UiO-66-PDMS	<i>Aspergillus niger</i> lipase	Soybean oil	88 %	24 h/45 °C	83.0 %, 10 runs	Centrifugation (10,000 rpm, 12 h)	[73]
Bio-Zn-MOF	Thermophilic lipase QLM	Sunflower oil	>60 %	50 °C	80.0 %, 5 runs	–	[72]

GA: glutaraldehyde, AP: 3-aminopropyl triethoxysilane, GO: graphene oxide.

NPs: nanoparticles, PDA: polydopamine, PDMS: polydimethylsiloxane.

MGO: superparamagnetic few-layer GO, PEI: polyethyleneimine, MOF: metal organic framework.

GO-Fe₃O₄: hybrid of few-layer graphene oxide and Fe₃O₄.

mCNTs-Fe₃O₄-PAMAM: carbon nanotubes filled with magnetic iron oxide and modified with polyamidoamine dendrimers.

Fe₃O₄ NPs-GO: magnetic Fe₃O₄ NPs encapsulated in GO.

P(GMA-coMAA): poly(glycidyl methacrylate-co-methacrylic acid).

ZIF-8: X-shaped zeolitic imidazolate frameworks.

CLEAS: cross-linked enzyme aggregates.

Lipase QLM: an extracellular enzyme from *Alcaligenes* sp.

2.1. Metal-organic frameworks-based nanobiocatalysts

Metal-organic frameworks (MOFs) are a subclass of organometallic polymers that result from the coordination of metal ions or clusters with organic ligands in the form of one-, two- or three-dimensional structures. The interesting feature of most members of MOFs is the unique structure porosity. Recently, the application of this group of advanced nanoparticles in the synthesis of nanobiocatalysts has been reported [70]. The presence of high surface area, open pores, and ideal pore size make these crystalline and highly porous compounds suitable for hosting different species, especially enzymes. Three different immobilization strategies have been used to stabilize enzymes in MOFs. In the first strategy, which is called the surface immobilization method, the outer surface of MOFs is used to stabilize enzymes. The second strategy, in situ encapsulation or bottle-around-a-ship strategy, involves forming an array of MOFs around the enzyme. The third strategy, or ship-in-a-bottle method, involves trapping enzymes in the pores of prefabricated MOFs [71]. In all of these approaches, the stabilized enzyme can be recycled and reused. However, to minimize the enzyme leakage issues and maximize resistance to degradation, the bottle-around-a-ship is considered the most appropriate way to reduce the cost of biodiesel production. Lee et al. [72] applied the biomimetic mineralization strategy to engineer L@Zr-MOFs nanobiocatalysts applicable for the

transesterification of sunflower oil. The manufactured nanobiocatalyst was stable during three consecutive cycles with no significant change observed in its structure. Hu et al. [73] used lipase enzyme immobilization on the surface of zirconium-based MOFs to fabricate a new nanobiocatalyst for the soybean oil transesterification process. The surface of the synthesized nanobiocatalyst was hydrophobically modified before enzyme stabilization by coating with polydimethylsiloxane using the chemical vapor deposition (CVD) method, and then hydrophobic interactions were used for enzyme immobilization. The use of the chemical vapor deposition method can create hydrophobic properties on the MOF surface and, at the same time, preserve the intrinsic properties of MOFs.

2.2. Metal oxide-based nanobiocatalysts

Metal oxides have been used successfully in the development of nanobiocatalysts for organic dye photocatalytic degradation [91], wastewater treatment [92], and upgrading recalcitrant lignocellulosic biomass hydrolysis [93–96]. However, their application in the energy recovery process is still a relatively rare investigated issue that requires the attention of researchers, and further detailed studies should be performed in this field. Fatima et al. [83] used covalent stabilization of the lipase enzyme on the surface of polydopamine-modified cerium

oxide nanoparticles to develop a new nanobiocatalyst for the transesterification reaction of *Eruca sativa* oil. Response surface methodology and gas chromatography–mass spectrometry techniques were used to optimize the reaction parameters such as catalyst mass percentage, oil to methanol ratio, water content, temperature, and time. They successfully produced biodiesel from non-edible *Eruca sativa* seed oil with 89.3 % yield after 30 h reaction at 35 °C. The developed nanobiocatalyst retained its stability for more than five reaction cycles. The enzyme was recovered by centrifugation.

2.3. Magnetic-based nanobiocatalysts

Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) [97] and magnetite (Fe_3O_4) [98] are two common types of colloidal ferrite that are known for their magnetic properties. The use of magnetic nanoparticles in the development of nanobiocatalysts used in energy recovery from resources has been more extensively considered and studied compared to other nanomaterials. The magnetic properties of the nanoparticles, the available synthesis, preparation and separation methods, the cost-effectiveness, the presence of suitable pores, porosity, and the high active surface area for enzyme immobilization make them eligible candidates for the nanobiocatalysts preparation. There are more reports on the development of nanobiocatalysts based on magnetite than maghemite. Magnetite nanoparticles require additional functionalization steps to modify their surface to prevent the loss of their exceptional properties on exposure to air oxidative reactions. In addition, magnetite nanoparticles are sensitive to acidic environments and have a mineral hydrophobic nature, which makes their interaction with biological components complicated [99]. Hence, various surface engineering techniques have been used to adapt the surface chemistry of these nanomaterials for the loading of biological materials.

The hydrophilicity of the surface of magnetite nanoparticles was boosted through functionalizing with carboxylic acid or amine groups that provided strong covalent bonds with the biological component and facilitated enzyme immobilization on their surface [100]. The most common process used in magnetic nanoparticle surface engineering is the surface functionalization process using amino silanes, especially 3-aminopropyl triethoxysilane (AP) and glutaraldehyde. Amino silanes have a hydrophobic end with a silicon-oxygen backbone and a flexible hydrophobic carbon tail. The hydrophobic part of silanes facilitates their binding to magnetic nanoparticles with the same nature. The good binding affinity of the amine group of amino silanes to the carboxylic acid groups leads to the amide bond formation and anchoring glutaraldehyde on the surface of magnetic nanoparticle. Glutaraldehyde creates a hydrophilic environment by creating free carboxylic acid heads that facilitates the absorption of biological structures [101]. Touqeer et al. [79] utilized the solvothermal method to synthesize polydopamine-modified magnetic nanoparticles. Then, lipase enzyme immobilization of the *Aspergillus terreus* AH-F2 on the surface of synthesized nanoparticles was done. The prepared nanobiocatalyst was catalyzed the transesterifying the waste cooking oil for biodiesel production. Costa et al. [101] stabilized the *Candida antarctica* lipase B enzyme on the surface of Fe_3O_4 nanoparticles modified with AP and glutaraldehyde to synthesize nanobiocatalysts effective in isoniazid synthesis.

2.4. Inorganic nanoscaffolds-based nanobiocatalysts

Nanomaterials based on carbon structures such as carbon nanotubes (CNTs) and graphene oxide (GO) as well as nanomaterials based on mineral nano-oxides such as alumina (Al_2O_3) and silica (SiO_2) are recognized as a class of widely used nanomaterials for production of nanobiocatalysts used in the recovery of energy resources. These rigid inorganic nanostructures offer numerous advantages over other nanomaterials for stabilizing biocatalytic components. These nanomaterials are commonly used with other nanomaterials, for example, magnetic

nanoparticles. The composition of GO with mineral oxide nanoparticles strengthens its structural resistance through the placing of nanomaterials between the empty spaces of a two-dimensional GO network, which in turn increases the resilience of the prepared composited nanobiocatalysts under process conditions. Zee et al. [88] used the composite of Fe_3O_4 nanoparticles and GO to covalently immobilize *Candida rugosa* lipase and prepare nanobiocatalyst used in soybean oil transesterification reaction. This nanobiocatalyst is able to support a maximum performance of 92.8 % under optimal conditions. Lee et al. [102] also investigated the effect of lipase immobilization on the GO surface and compared the results of the immobilized and free enzymes in terms of enzyme activity. The results showed that the activity of GO-immobilized lipase was much higher than that of free enzyme. This study identifies GO as exceptional support for lipase immobilization. GO, with its two-dimensional plates and honeycomb arrangement of carbon atoms, is able to provide a very high surface area for enzyme immobilization. In addition, the high mechanical strength and availability of two-dimensional surfaces, as well as the presence of epoxy, hydroxyl, and carboxylic acid functional groups, provide suitable conditions for surface chemistry engineering and successful immobilization of lipase enzyme without the need for complex surface modification through expensive reagents and multi-steps process [78]. So far, various immobilization methods, such as entrapment in GO structure, physical adsorption, and covalent bonding for the development of GO-based nanobiocatalysts have been reported [102].

CNTs are also among the most widely used mineral nanostructures used for nanobiocatalysts synthesis. The inertness, biocompatibility, excellent thermal stability, high surface area, high mechanical stability, and high enzyme loading capacity are benefits of CNTs [103–105]. Enzymes can be stabilized on the surface of CNTs through a variety of physical binding and covalent bonding methods. CNTs can also be used to stabilize enzymes with or without surface modification [85,106–114]. For example, enzyme immobilization by physical adsorption mechanism on single-walled carbon nanotubes does not require surface chemical modification strategies [114]. The lipase immobilization on CNTs via hydrophobic interactions produced a nanobiocatalyst with outstanding stability and efficiency for biodiesel production [113]. Das et al. [108] chemically modified the surface of a GO-CNT composite employed for cross-linking of glutaraldehyde and then immobilization of β -amylase enzyme. The fabricated nanobiocatalysts showed improved biocatalytic stability and performance.

Al_2O_3 and SiO_2 are two examples of mineral nano oxides used to synthesize nanobiocatalysts. To the best of our knowledge, there are a considerable number of studies using SiO_2 to prepare nanobiocatalysts in biodiesel synthesis. Nevertheless, similar studies on the use of Al_2O_3 are limited and investigation in this field needs significant expansion. Guardi et al. [115] prepared and evaluated the efficiency of $\text{SO}_4/\text{Fe}_3\text{O}_4\text{-Al}_2\text{O}_3\text{-TiO}_2$ nanocatalyst for biodiesel production by transesterification of cooking oil waste. They achieved 96 % production efficiency for the fatty acid methyl ester. Ashjari et al. [116] investigated the application of multicomponent reaction for covalent stabilization of two lipases (*Thermomyces lanuginosa* and *Rhizomucor miehei*) on aldehyde-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ magnetic nanoparticles under mild conditions. The produced nanobiocatalyst was used to produce biodiesel from cooking oil wastes by the transesterification method. By optimizing the reaction conditions, the efficiency of biodiesel production reached 93.1 % with the possible reuse of the nanobiocatalyst in five reaction cycles. Fathi et al. [117] used silica nanoparticles modified with (3-aminopropyl) triethoxysilane (APTES) for non-covalent stabilization of *Yarrowia lipolytica* lipase without adding any binders or precipitating agents. The longer stability resulted from their nanobiocatalyst at higher temperatures and neutral pHs compared to the one prepared by metal chelates immobilization strategy.

Nanobiomaterials are composed either of natural or synthetic nanomaterials containing wholly or partially of biological molecules such as plant extracts, microbes, virus, polysaccharides, or proteins.

They are applicable in diverse fields, namely tissue engineering, nanomedicine, drug delivery, bio-imaging, and nanobiocatalyst. Metal-organic frameworks, metal oxide nanoparticles, magnetic nanoparticles, carbon-based and inorganic nanostructures are five crucial classes of nanoparticles employed in the development of nanobiocatalysts utilized in energy production through transesterification for resource recovery.

In the next section, we will discuss the advantages of nanobiocatalysts and how their stabilization in the nanostructures improves their efficiency and stability.

3. Advantages of nanobiocatalysts

There are restrictions on the use of the enzyme separately and freely. For example, high production cost, reduced stability toward a wide range of temperatures and pH, poor recovery, limited activity range, scant stability in industrial scale and conditions, and prone to deterioration are some of the problems with using free enzymes. Enzyme fixation on suitable carriers can lead to outstanding benefits. While the price of a final stabilized enzyme-based catalyst is cheaper, the enzyme stability is improved after immobilizing and can be easily employed in various reaction and production conditions [118]. Easy recovery of the enzyme and thus reusability in subsequent processes is possible. Enzyme activity is regulated and enhanced. By easily recovering the enzyme from the reaction medium, a purer, enzyme-free product can be simply acquired. The kinetic variables of the enzymatic reaction are accelerated.

The field of nanotechnology is expanding rapidly. The nanomaterial dimensions provide outstanding advantages, such as a very large active surface area and huge surface-to-volume ratio as a substrate for enzyme stabilization. With the help of porous nanomaterials, as a stabilizing substrate for biocatalysts, the synthesis method becomes easier. Moreover, with small amounts of enzymes, more active and permanent nanobiocatalysts can be prepared. The nano-property helps the active sites of the enzyme to be more exposed to the desired reaction, while the active part remains stable and prevents the denaturation of the biological components and the degradation of the enzyme structure.

The magnetic CNTs with the necklace-shape nanostructures were hydrothermally synthesized [119]. Then, the various functional moieties were attached on the s CNTs surface by the hyperbranched poly(amidoamine) through the Michael addition reaction. The final functionalized magnetic CNTs were utilized as proper support for the conjugation of the glucoamylase enzyme via multi-interaction processes of the adsorption, covalent attachment, and metal-ion affinity. This enzyme fixation process on the CNTs is reversible and recyclable, which dramatically reduces the amount of enzyme required and the preparation cost of the nanobiocatalyst. The developed immobilizing strategy provided superior thermal and pH stability and reusability, without compromising the substrate specificity of free glucoamylase. High enzyme stabilization capacity, enzyme recovery and reuse, and support regeneration are the prominent advantages of the produced nanobiocatalyst.

The poly(amidoamine) dendrimer is a potential carrier for enzyme stabilization in nanobiocatalyst structure [120]. Perfect molecular framework, supreme geometric symmetry, large number of available functional groups at the end of dendrimer branches, biocompatibility and lucrative chemical affinity are attractive features of poly(amidoamine) dendrimer. The poly(amidoamine) grafted onto the silica surface (G3 PAMAM-grafted silica) via microwave irradiation using glutaraldehyde as the cross-linking agent was utilized as a proper support for cellulase fixation. The enzymolysis performance of the carboxymethyl cellulose by immobilized cellulase onto G3 PAMAM-grafted silica was boosted as it showed higher stability and activity under a wide range of thermal and pH conditions. In 2016, a solvothermal reduction procedure was applied for grafting the poly(amidoamine) onto the Fe₃O₄ microspheres, which utilized as a strong support for *candida rugosa* lipase

immobilization [121]. This immobilizing strategy was eco-friendly and facile. The synthesized nanobiocatalyst had the advantage of reactivation of inactivated immobilized lipase via glutaraldehyde and copper ion addition, respectively, Fig. 1. The catalytic activity and reusability of this nanobiocatalyst were evaluated in 10 cycles, which achieved elevated catalytic performance with the enzymatic activity retention >90 % besides longtime storage stability.

Nanomaterials provide a wide active surface area, high stability, resistance and increased catalytic activity for the biocatalyst. Integrating magnetic nanomaterials with nanocatalysts has made nanobiocatalysts recoverable and reusable. Therefore, the high operating costs associated with the production of enzymes and the synthesis of nanocarriers are offset and bring economic benefits. The application of nanobiocatalysts has provided the benefits of long-term stability, greater catalytic activity and efficiency, greater selectivity, easier operating conditions, and cost-effectiveness. In the following, the developed strategies for the preparation of nanobiocatalysts will be reviewed.

4. Processes of nanobiocatalysts production

Enzymes or biocatalysts are highly effective compounds that allow a reaction that does not occur simply under normal conditions to occur and increase the process rate. They are natural-based compounds that are not consumed in the reaction but provide a lower energy path for the reaction to take place. Biocatalysts are active in different conditions of temperature and pH range and can act at atmospheric pressure under various heat and acidity situations. Most of their optimum performance is at a temperature of 37–70 °C and a pH close to neutral. Today, special biocatalysts have been developed that operate at higher temperatures and in particular applications. These biocatalysts are produced using genetic engineering and protein engineering methods. They are made from natural systems that can be easily absorbed into nature if they are broken down into the components from which they are made with no risk to the environment. Enzyme stability is needed to expand their use in laboratories and industries, as well as to ensure their reuse in production. Short life, low stability, high cost, difficult recovery, and laborious purification process are the main limitations of enzymes. In addition, a significant problem in the industrial use of enzymes is the difficulty of their separation from the reaction medium and inactivation in organic solutions at unusual temperatures and pHs.

Enzymes engineering is actually the modification of enzymes in a way that improves their performance. In recent years, various materials such as metal nanoparticles, polymeric materials, silicate, and carbon-based materials have been used to engineer enzymes and increase their efficiency. Newer designs use stabilized enzymes to facilitate segregation and allow them to be used in continuous bioreactors to reduce process costs. The enhancement of the enzyme stability by the immobilization process has been practically observed and theoretically confirmed. Interestingly, the enhancement of the enzymatic activity has been observed in some cases after immobilization. Immobilization methods include adsorption, covalent bonding with a substrate, enzyme-enzyme crosslinking, trapping, and encapsulation.

One of the capable approaches for enhancing enzyme performances is the immobilization of the enzymes on nanostructured materials that led to the production of the nanobiocatalyst. A nanobiocatalyst is an emergent invention that generally blends nanotechnology and biotechnology breakthroughs. The organization of nanobiocatalyst involves the collecting of enzyme molecules onto nanostructured carriers to create selectivity for substrates and errand eligible chemical kinetics. The functionalization of nanostructures assembles enzymes into stable structures, which can work as a processing machine and nanoscale information storage. According to studies, large surface areas of nanostructured materials in the nanobiocatalysts decrease mass transfer insistence and provide a higher enzyme loading for substrates. Variant nanomaterials are used for the expansion of nanobiocatalyst, such as nanofiber scaffolds [122], nanoparticles [123], nanotubes [124],

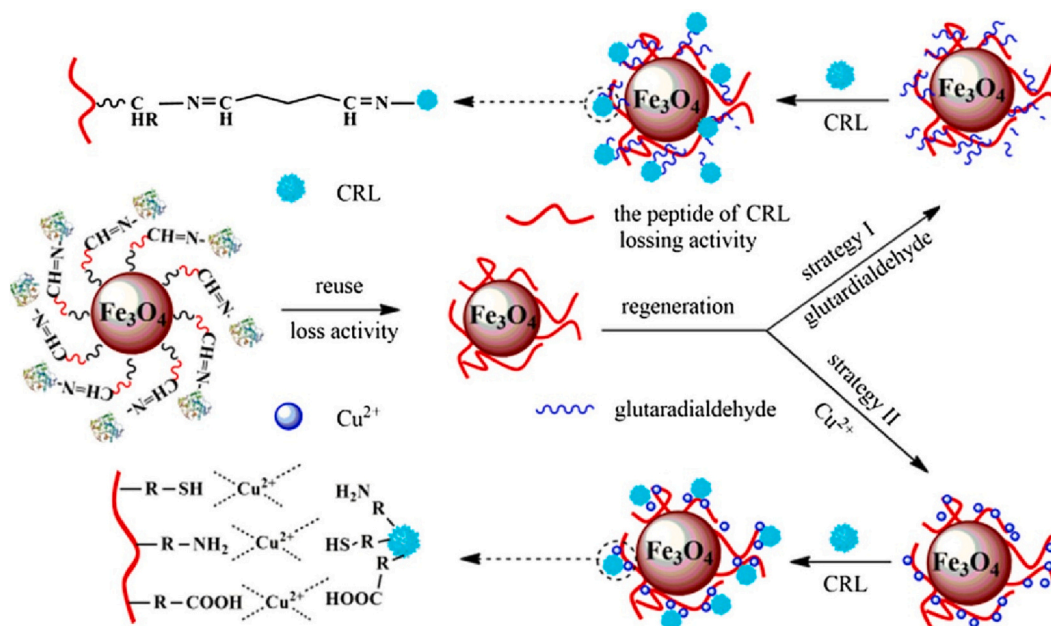


Fig. 1. The strategies for regeneration of the magnetic PAMAM carrier. PAMAM: Poly(amidoamine), CRL: *Candida rugosa* lipase. The enzymatic activity may be reduced during successive use due to not attachment of some particles to the support and the lipase disserve from the support. The nanobiocatalyst regeneration can be performed through the attachment of CRL to the PAMAM with the help of glutaraldehyde or copper ions. Reprinted from Ref. [121] with permission from Journal of Nanoparticle Research.

nanosheets [125], and nanocomposites [126].

Immobilization methods of nanostructured biocatalysts are classified into three groups based on applied synthetic methods: self-assembly, grafting onto, and grafting from. In the grafting onto procedure, enzymes are immobilized on nanoparticles or nanofibers. In the grafting from approach, grafting is done from enzymatic macromonomers or enzyme macroinitiators. The self-assembly method is based on the direct enzyme-polymer amphiphilic interactions or enzyme grabbing onto polymer aggregates. The preference of these methods is determined based on their ability to enhance the stability of the enzyme in reverse conditions, their potential for large-scale enzyme preparation, and their application as nanostructured biocatalysts. Immobilization mechanisms are based on the volume and size of the holes, load interactions, hydrophobic interactions, and multi-point connections based on the restriction and confinement of enzymes. Nowadays, special attention is paid to new methods for designing and synthesizing nanostructured biocatalysts, including molecular imitation and molecular insight into the construction and application of nanostructured biocatalysts. Commonly, a molecular template is required for the design and application of nanostructured biocatalysts.

The metal, polymer, carbon, or silica-based substrates are employed for the synthesis of enzyme based-nanobiocatalysts. Polymers are usually suitable for enzyme immobilization because their surface can be modified. Due to the usability of these materials in a nanoform, excellent surface area are exposed for enzyme immobilizing [127]. The vast and adjustable surface of polymers enables the enzyme loading for various applications [127–129]. Carbon-based biocatalysts, including carbon nanotubes, graphene, and nanodiamonds, have been widely used for enzyme immobilization due to their high thermal stability, ineffectiveness and biocompatibility [8]. Silicon-based substrates are very interesting because enzymes can be physically adsorbed on them through electrostatic and hydrophilic/hydrophobic interactions. The attributes of silicate substrates, such as surface charge density, pore geometry and functional groups in mesoporous silicates, are variable and this ability helps to adsorb a variety of enzymes [130–132].

There are some exciting competencies in metal-based nanocarriers of enzymes. By creating functional groups, such as carboxylates, amino

acids, thiolates, or phosphates on the surfaces of metal nanoparticles, these substances can react vigorously with enzymes. Such strong immobilizing of the enzyme on metal substrates improves the biocatalytic performance and stability [133]. It used hydrophobic interactions, electrostatic interactions, hydrogen bonding, van der Waals forces, chemical bonds, such as covalent bonding, enzyme crosslinking, or physical entrapment or encapsulation. Fig. 2 shows the synthesis approaches of nanocarriers and the immobilization strategy of enzymes to perform a specific function of the nanobiocatalyst. The right strategy for enzyme immobilization depends on several factors. These factors include the molecular structure of the enzyme, the site of application, functional groups of nanocarriers, the required activity and stability, and selectivity.

In general, there are three strategies for the development of new nanocarriers and the improvement of enzyme immobilizing process. (i) Introduction of functional groups on the surface of nanomaterials, (ii) utilization of the structures effective in the surface area enhancement, substrate dispersion, recovery of nanocarriers or encapsulated enzymes entrant nanocages, (iii) improve the thermal and mechanical stability of nanocarriers. Accordingly, different types of progressive nanocarriers have been reported and developed in recent research, such as nanoparticles, nanospheres, nanogels, nanocages, nanowires, nanocubes, nanorods, nanofibers, nanotubes, nanofilms and nanosheets [134].

Three main methods employed to immobilize biocatalysts in the nanostructured materials are grafting onto, grafting from, and self-assembly. The metal, polymer, carbon, or silica-based substrates are mainly utilized for the synthesis of enzyme based-nanobiocatalysts. Here, the diverse attachment forces applicable for enzyme immobilization are reviewed.

4.1. Physical interactions

The most common method of enzyme immobilization onto the nanostructures is the physical adsorption via weak van der Waals forces. A severe problem of the physical adsorption-based prepared nanobiocatalysts in biological applications is enzyme leaching that prevents its implementation on an industrial scale [114,135]. The immobilization

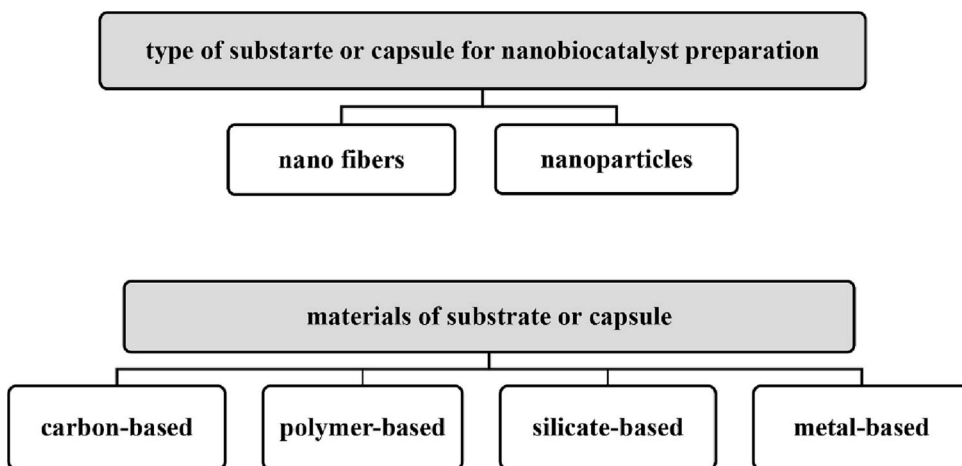


Fig. 2. Demonstrates nanobiocatalysts types, materials, and immobilization methods. The synthesis approaches of nanocarriers and the immobilization strategy of enzymes are important effective on the nanobiocatalyst performance for as a specific function. The right strategy for enzyme immobilization depends on several factors, including the molecular structure of the enzyme, site of application, functional groups of nanocarriers, the required activity and stability, and the selectivity. Immobilization methods of nanostructured biocatalysts based on used synthetic methods are classified into three groups: self-assembly, grafting onto and grafting from.

immobilization methods of enzymes	physical	
	self assembly	
	encapsulation	
	covalance bonding	complexation
		cross linkage
		chemical modification
	enzymatic macromonomer	
grafting	grafting from	
	grafting onto	

strategies are deeply dependent on the chemical and physical properties of nanocarriers and enzymes and their surface interactions. Some examples of physical adsorption methods, including hydrophobic, hydrophilic, π - π , and electrostatic interactions for the nanobiocatalysts preparation, are summarized in follow.

Enzyme molecules bind to the CNT surface through hydrophobic or π - π interactions. The horseradish peroxidase was set on a modified CNT with 1-pyrene butanoic acid succinimidyl ester [136]. The perhydrolase S54V was fixed on a modified CNT by a polyethylene glycol-based interceptor [137]. The electrostatic adsorption of lipase on the CNTs surface as well as the hydrophobic interactions, led to a more vital enzyme immobilization [113]. In this case, the duration of complete absorption of the enzyme depends on the average ionic strength. Hydrophobic amino acids in lipase caused the enzymes to be located in the open positions [138], which is a driving force to initiate the adsorption procedure. Graphene is another promising carbon carrier, which is physically adsorbed similarly. The glucose oxidase and glucoamylase have been physically immobilized on the chemically reduced graphene oxide carriers [139]. The enzymes can be physically adsorbed on porous silica carriers. For example, electrostatic adsorption of urease and α -amylase on bilayer alumina silicate nanotubes has demonstrated promising reusability and stability. After seven continuous cycles, reaction and isolation, both enzymes hold >55 % of their original activity. They retained >90 % of their activity even after 15 days of storage [130–132].

Another enzyme carrier used in the enzyme encapsulation process is organic-inorganic composite. This material has successfully immobilized enzymes such as alpha-lactalbumin, lactase, carbonic anhydrase,

and lipase. Enzymes showed higher enzymatic activity and stability within hybrid nanogels than in their free state. The porous structures of nanoparticles can provide a high surface area to enclose a large amount of enzyme. The pore size of nanoparticles is a critical parameter in the enzyme load, so the closer these pores are to the enzyme size, the greater the thermal stability of the enzyme. Smaller pores reduce enzyme loading, and larger pores reduce enzyme stability in cavities and leaks. Notably, the immobility in nanoparticles is physical and there is no link between the enzyme and the carrier surface. Recently, Du et al. [130] developed hierarchical porosity-like silica nanoparticles with a variety of controllable pores applicable for enclosing molecules of various sizes (Fig. 3).

Nanostructures containing pores and porosity can be combined with other materials as composites leading to a synergistic effect in their performance. For example, the hybridization of mesoporous silica nanomaterials with magnetic nanoparticles makes their recovery more feasible from the aqueous medium. Physical modification has low stability due to weak interaction between enzymes and nanostructures, which makes it necessary to modify the surface of substrate, enzyme, or both. In the following, the non-physical interactions are discussed.

4.2. Chemical bonding

The covalent attachment among the bonding mechanisms is exceptionally dependable for specific bonding places and circumventing enzyme leaching. Jiang et al. [140] chemically bonded lipase enzyme on magnetic nanoparticles. After 30 cycles of retention and separation reaction, nanobiocatalyst save 85 % of their original activity. The

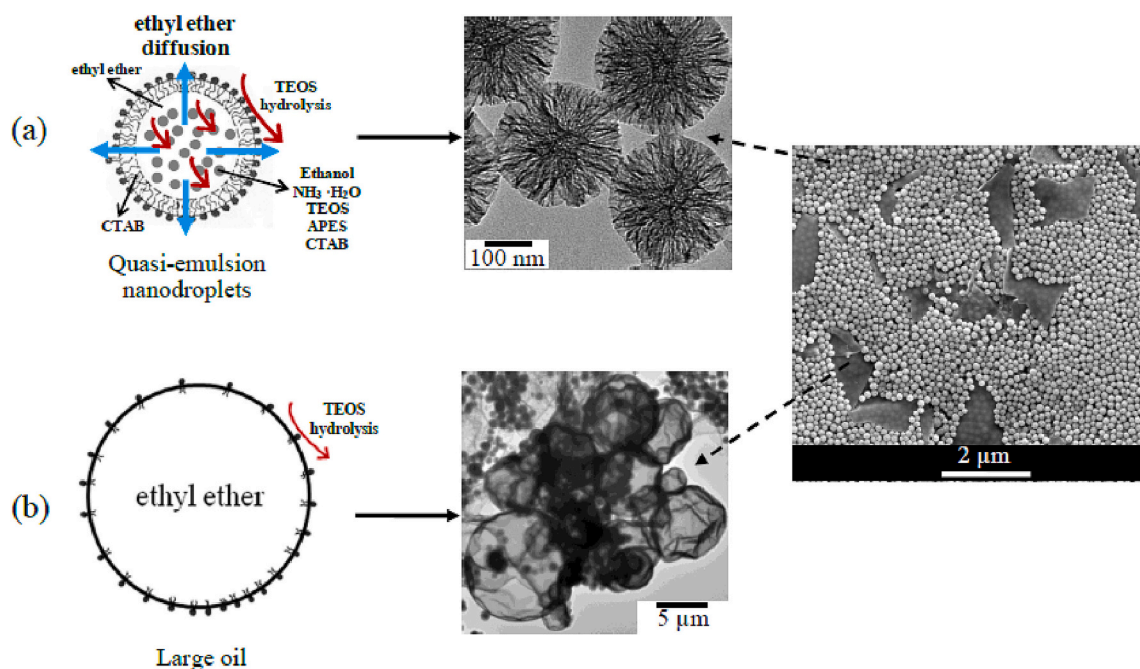


Fig. 3. The possible formation mechanism of dendrimer-like amino-functionalized silica nanoparticles with hierarchical pores particles and by-products. Reprinted from Ref. [130] with permission from Advanced Materials.

chemical nature of dendritic polymers with high thermal stability is ideal for the stabilization of high-density enzymes. Ge et al. [141] have bound lipase to the aromatic polyamide made of trimesic acid & phenylenediamine with a high molar ratio of enzyme to polymer up to 5–6. The superior stability has been achieved at high temperatures in the presence of organic solvents for lipase immobilized on the dendritic polymer. The existence of hydrophilic carboxylic groups on the polymer can create suitable microenvironments for lipases.

Wang et al. [142] immobilized α -chymotrypsin enzyme on polystyrene nanofibers. They reported that the enzyme maintained its hydrolytic activity up to 65 %. The half-life, an indicator of enzyme stability, was amplified about 18 times for the stabilized enzyme in methanol anhydrosis. The immobilized enzyme showed a transesterification activity 5670 times higher than the natural enzyme suspended in isoctane at 18 °C. These enhancements originated from the porous structure and the hydrophobicity nature of nanofibers, which facilitate the transfer of hydrophobic substrates to hydrophobic solvent. Another study about covalently cross-linked chymotrypsin aggregation on the polystyrene showed a 9-fold increase in enzyme activity. Here, the chemical composition of the protective carrier surface was well established by the design of polystyrene fixed on the nanofiber. However, to exploit the full potential of nanocarriers, it is necessary to understand the molecular level of the interactions between the enzyme and its microenvironments and their impact on the catalysis of a particular substrate [143–145].

Covalent binding of enzymes to CNTs carriers requires introducing functional groups such as amines or carboxylic acids to the carrier surface [146]. Lipase [103], organophosphate hydrolase [147], and other enzymes have been successfully immobilized on covalently functionalized CNTs. The other carbon-based nanostructures display similar physical and chemical properties to CNTs. Trypsin was immobilized by covalent bonding on blown nanodiamonds (3 to 10 nm) [148].

Metal nanoparticles are also good options for the covalent immobilization of enzymes. Fe_3O_4 -chitosan magnetic nanoparticles were used to fix the lipase, utilizing the EDC/NHS (N-ethyl-N'-(3-(dimethylamino) propyl)carbodiimide/N-hydroxysuccinimide) coupling agents. Mahmoud et al. reported [149] similar binding techniques for the immobilization of cyclodextrin glucan transferase on cellulose nanocrystals.

Carbohydrates or polyethylene glycol can be used as a binding agent for the surface of the enzyme, in which case, in addition to covalent bonding, the presence of hydrogen bonding helps to immobilize the enzyme better [150]. In this case, Stoilova et al. [151] used a copolymer to bind acetylcholinesterase. They optimized various conditions, including the weight ratio of the two polymers, to obtain a significant amount of active anhydride moieties and obtained satisfactory results from enzyme stabilization. One advantage of using polymers as bonding intermediates is that the reaction with polymers such as polyether creates a gap that allows the enzyme to move and minimizes spatial interference. This contributes significantly to the storage and thermal stability of the enzyme at the site.

To increase their biocompatibility, the polymer surfaces can be modified. Polyacrylonitrile is a nitrile-rich polymer that can be modified by imidoesterification and then efficiently bind to amino groups of enzymes. This conjugation was not efficient enough because its initial activity was reduced after 10 repeated cycles to <30 %. Li et al. [152] developed a solution for growing the efficiency of the mentioned conjugation. They used an epichlorohydrin-coupling agent for conjugating catalase onto polyacrylonitrile nanofibrous, which improved the immobilization of enzymes. It was a non-toxic and more effective cross-linking agent.

Nanogels are cross-linked nanoporous particles produced from hydrophilic polymers. Nanogels are also a good option for covalent immobilization of enzymes. The enzyme α -chymotrypsin was immobilized on porous magnetic nanogels by photochemical in situ polymerization [153]. This enzyme was ligated to the carboxyl group by activating 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide. Moreover, the simultaneous immobilization of two or more enzymes on the surface of nanogels is possible. Alternatively, in situ polymerization can be performed in the presence of enzymes to create a porous polymer network. So, the enzyme can quickly attach on the surface of the substrate with less permeability [154]. The polymers surface modification not only provides proper bonding sites for the enzyme, but also expands its surface area. Treatment with oxidizing agents like sulfuric acid and nitric acid has been reported in this case. The fine-tuning of the porous structure of the polymer for facile diffusion of biomolecules and their uniform distribution deeply depends on the chemical modification.

Another way is the encapsulation of enzymes in the nanogel. The porous structures of nanogels are commonly used to overcome poor mass transfer in nanogels (Fig. 4) [155].

Another way to immobilize the enzyme is by utilizing an intermediate, called the spacer arm, between the enzyme and the activated substrate. For example, such a spacer arm is created by activating an amine using glutaraldehyde as a coupling agent or carbide imid derivatives. Although these bridge molecules or binding arms significantly reduce the leaching rate of the enzyme, they may also reduce the biological activity of the enzyme due to the strong binding. Zhang et al. [131] functionalized silica nanoparticles with aldehyde, cyanogen, epoxy, or carbide imide groups and studied their enzyme immobilization. The results show that aldehyde and epoxy-activated silica particles can react with the -COOH and -NH₂ functional groups in the lysine residue of the enzyme. Such changes were applied to immobilize *Rhizobium etli* CFN₄₂ xylitol dehydrogenase to synthesize numerous rare sugars. In another study, researchers experimentally proved that laccase immobilization improved by available functional groups such as oxirane rings, -OH and, -NH₂ [156].

Affinity binding is also used for bioconjugation onto supports. For example, grafted ferric silica nanoparticles by alkyl groups were conjugated with lipase with a binding efficiency of up to 97.9%. Therefore, the enzyme stability is enhanced by conjugation without significant loss of its transesterification action. The enzyme binding via affinity grafting can occur by adding metal ions onto the substrate surfaces. One example is the improvement of attachment of lactase onto mesoporous silica containing Cu²⁺ [135]. Copper and nickel were utilized to modify silica for lipase protease inhibitors [157] and bind His-tagged [158].

Among metal-based nanocarriers, magnetic nanoparticles are an extraordinary example owing to their great reusability and ease of separation. These nanomaterials can be functionalized by amino, carboxylate, thiolate, or phosphate to create strong interfacial reactions with enzymes. These composites increase both biocatalytic performance and enzyme stability [133]. Cofactors or multi-enzymes may be attached to nanoparticles, because multi-functional groups can be loaded on single-metal nanoparticles. These multi-enzyme structures facilitate multi-reaction in a one-pot medium by shortening long reaction pathways [159]. Modified Iron (II, III) oxide nanoparticles by robust silane linkages [160], enzyme horseradish peroxidase, mediator thionine, and secondary anti-human IgG antibody are examples of multi-enzyme nanobiocatalysts.

It is also possible to coat the surface of metal nanoparticles with a thin layer of polymers and then use functional groups for the stable immobilization of enzymes. Polyvinyl alcohol, chitosan, polyethylene glycol, and polyethyleneimine have been used so far [161]. Targeted immobilization on metal nanoparticles by the polymer coating (such as antibody-antigen) can also be achieved through affinity interactions. In one operation with this strategy, at first, biotin groups were attached to metal nanoparticles, and then streptavidin was attached to biotin-coated

nanoparticles. Another example is the catalase immobilization on gold-coated nanoparticles [162] and glucose oxidase on apoferritin nanoparticles [163]. Peptides can also be used to modify metal nanoparticles surface. One example of a metal-binding peptide is the gold-binding peptide [164]. Moreover, ligands can be utilized to bind peptides to metal nanoparticles better. Metal nanoparticles can be composited with CNTs, mesoporous silicas, and polymer nanogels, or nanofibers.

4.3. Grafting

The “grafting onto” method is performed in two reaction steps. Synthesis of nanocarriers is the first step, for example, polymer nanocarriers and nanowires, magnetic nanoparticles, and nanoparticles of cadmium sulfide, silver, alumina, and silica. Immobilization of the enzyme on the surface of the nanocarriers using a suitable strategy is the second step. Enzymes immobilized by this method include chymotrypsin, beta-lactamase, lysozyme, fungal protease, pepsin and catalase [86,165–167]. “Grafting from” is the in-situ growth of polymer chains on the enzyme surface. In most cases, enzymes are modified to produce the reactive groups needed for subsequent polymerization. Its main difference with “grafting onto” is the combination of all reactions involving the formation of nanostructures and the binding of the enzyme in a step. Compared with the “grafting onto” method, in which the bonding reaction between the enzyme and the carrier often results in spatial inhibition and leads to low enzymatic bonding efficiency, the “grafting from” method ensures high efficiency of the enzymatic encapsulation for high bonding efficiency of the enzyme and small molecular monomers. Some of the enzymes that have been stabilized by this method are alpha-chymotrypsin, peroxidase, lysozyme, and bovine serum albumin [142,168–170].

4.4. Bonding of enzymatic macromonomers

Wang et al. [171] worked on the in-situ polymerization of the enzymes, which is the first stage in the formation of a double bond on the surface of the enzymes. The formation of enzyme macromonomers and then polymerization by enzyme transfer were progressed in the organic phase followed by pairs of surfactant ions. The prepared biocatalysts were stable in both organic and aqueous media. Kim & Grate [172] prepared enzyme-nanoparticles with different nanometer diameters while their stability was greatly enhanced.

4.5. Self-assembly

Biological and environmental applications of nanobiocatalysts require enzymes applicability in structures without additives and changes in performance. By applying modern engineering methods and the development of modification procedures, nanobiocatalysts with biochemical functions should be justified with the aim of increasing the

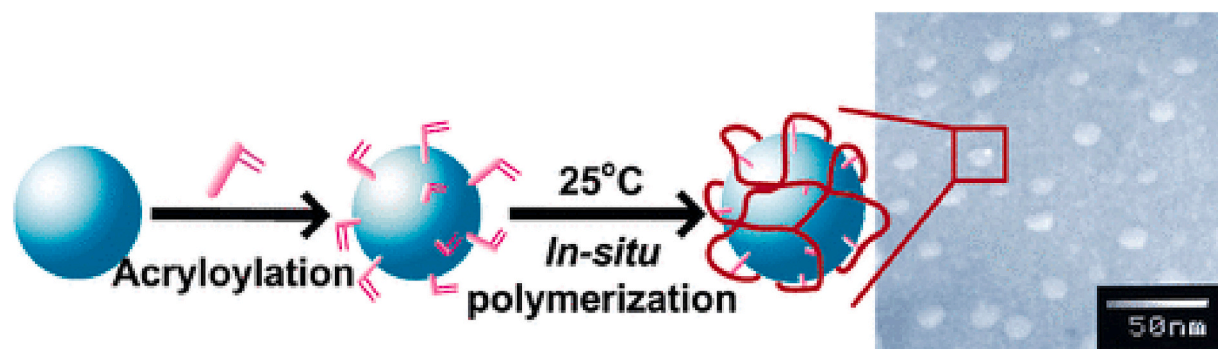


Fig. 4. Single proteins encapsulated into nanogels with uniform size and controllable shell thickness were prepared by surface acryloylation of a protein molecule followed by aqueous in situ polymerization [155] with permission from Journal of American Chemical Society.

activity and stability of the enzyme, as well as reusability and processability. One of the exciting materials for immobilizing enzymes with the mentioned conditions is the employment of nanostructured fiber. These materials provide homogeneous dispersion and high enzymatic loading in the liquid phase, significant porosity, and cross-linking, known as barriers to mass transfer. Nanofibers with discrete nanostructures, specific surface properties, and self-assembly behaviors give exciting opportunities for nanobiocatalyst development in biological processes as bioreactor systems. Electrospinning is a common technique for integrating enzymes into nanofiber structures due to its simplicity. In addition to single-fiber configurations, composite structures such as laterals, core shells, and hollow nanofibers can be fabricated and used to immobilize enzymes [173]. The electrospinning technique can also be used to make inorganic/organic hybrids. Hybridization of minerals with desired features improves the strength of the structure and allows these nanobiocatalysts to be used repeatedly. For example, silica nanoparticles inside hollow polymer fibers were used to synthesize nanocomposites [174,175]. The hybrid nanocomposite can tolerate shear strain through bioprocessing without great deformation. Huang et al. [176] found out that the uniform distribution of quantum dots on polymer nanofibers results in a higher degree of compaction and stiffness, which leads to efficient enzyme immobilization.

4.6. Encapsulation

In addition to the fact that enzymes can be immobilized on the surface of substrates, they can be trapped inside the pores of nanostructures. Similar to surface immobilization in the encapsulation method, enzyme leaching can be a major issue, especially when the enzymes are tightly bonded by physical adsorption. However, chemical adsorption also raises problems. The non-physical adsorption of the enzyme can be affected by structural changes, or enzymes activity can be reduced by exposure to cross-linking reagents. Electrospinning can be used to encapsulate enzyme molecules. In this method, encapsulation of enzymes is attained by cross-linking the polymer or *co*-electrospinning with an aqueous enzyme in the core and the formation of a water-insoluble shell by the polymer [177]. Mesoporous silica with spherical mesocellular cages can also be used for this purpose. These nanoshells can be made up of biological molecules such as DNA through the self-assembly process of DNA. Numerous cage structures can be formed by DNA molecules, including quadrilaterals, cubes, octagons, duodenum, and icosahedral shapes [178].

The application of technologies based on nanobiocatalysts is still in the early stages of entering the resource recovery industry. The mechanisms of nanobiocatalysts action and required properties to enter the field of industrial processes will be discussed in the next part.

5. Resource recovery

Toxic pollutants that come from industries, domestic, and agricultural wastewater, such as nitrogen and phosphorus-based fertilizer and pesticides, constantly affect the environment and human health. Both traditional and advanced methods are employed for the treatment of environmental pollutants [179]. Nevertheless, resource constraints change current social production systems and replace wastewater treatment with resource recovery. Biotechnological processes provide an economical way to concentrate and convert resources from waste or wastewater to valuable products. Biogas (biomethane) and biohydrogen as bioenergy sources have been classic goals, according to which the direct conversion of waste biomass as a carbon source to biodiesel has been considered. Another way for carbon recovery is the use of methane, hydrogen, and organic acids for manufacturing worthwhile biopolymers. In addition to the inherent human and environmental concerns about toxic metals, nitrates, pesticides, and plastics contamination, there is an expanding opportunity to recover and reuse these resources [180]. In the following, the recovery of these toxic

substances is described.

5.1. Recovery of toxic metals

Metals play a very important role in nature, human life, and industry. There is a wide range of diverse applications for all types of metals [181–183]. Meantime, indiscriminate harvesting of natural resources and non-recycling of waste is a serious risk for both industry and human health, and in total biological balance in ecosystems and human welfare. Therefore, along with the development of various metals-based technologies, it is necessary to develop high-performance and efficient processes for the metal recovery and return to the production cycle [184,185].

Based on the toxicity and physiological impact, different types of metals are divided as low (iron, molybdenum, and manganese), medium (zinc, nickel, vanadium, copper, cobalt, chromium, and tungsten), and high (arsenic, antimony, silver, mercury, cadmium, mercury and uranium) impact, which are harmful to humans and the environment [186–190]. The treatment of wastewater is drawing special attention as the accumulation of pollutants in the ecosystem affects the food chain [191]. In the meantime, toxic metals have a major impact on human health once they enter the human body through the food chain. Metal recovery has been studied by various techniques, including physical (adsorption, coagulation, and flocculation) [182,183,190], chemical (ion-exchange, photocatalysis), and biological (biosorption, bioaccumulation, oxidation/reduction, leaching, precipitation, volatilization, degradation, and phytoremediation). Physical and chemical methods of removing toxic metals have disadvantages such as high operating costs, production of large volumes of metal-rich sludge, and difficulty in treating large volumes of wastewater containing low concentrations of toxic metal [192]. Biological methods, in comparison with physical and chemical methods, are one of the most effective environmentally friendly tools for the treatment of industrial effluents contaminated with toxic metals [193]. Table 2 shows the studies performed on the recovery of metals from waste and wastewater sources using various biological technologies. The whole cells of lead-resistant bacterium *Acinetobacter junii* L. Pb1 isolated from a coal mine dump when loosely associated with exopolysaccharide showed high binding affinity to Pb ion. Notably, each g of this absorbent effectively removed 1071 mg Pb ion [194].

5.2. Recovery of phosphorus from wastewater

For the past 60 years, the use of synthetic phosphorus (P) fertilizers has been multiplied, constantly harming the environment. Phosphorus contamination routes are numerous, including the discharge of wastewater treatment plants (urban and industrial), agricultural fertilizer losses (as a result of erosion, water runoff, and surface drainage), surface runoff of rainwater, leaching of phosphorus fertilizers including calcium phosphate derived from phosphate rock [202]. Accumulation of phosphate in water causes more growth of algae and aquatic plants and, as a result, decreases the oxygen content of water. Therefore, it disturbs the biological balance of water [203]. Despite efficient methods such as biodegradation or membrane separation, due to their costly process, the cheaper method based on ion-exchange adsorption is often used [204]. Rabiul Awwal prepared a mesoporous silica-based composite embedded with a selective ligand for phosphate ion adsorption from wastewater [203]. The hydrogen bonding and electrostatic interaction, along with ion-exchange process, helped to reach an adsorption capacity of ~159 mg/g. Shahat et al. modified the surface of UiO-66 (a well-known Zr-based MOF) with cationic surfactant N-Dodecylpyridinium chloride. Then, they impregnated the modified MOF surface with ammonium molybdate to prepare a selective phosphate adsorbent with ~70.5 mg/g adsorption capacity [205].

In this regard, technologies that provide the possibility of eliminating, recycling, and reusing phosphorus from polluted streams are

Table 2
Toxic metal recovery from wastewaters using various biological technologies.

Metal	Sample	Reaction/ microorganism	Recovery (mg/g)	Refs.
Ni (II)	Ni-containing industrial wastewater	Modified biochar by KMnO_4/KOH (MBC)/ Ni (II)	87.15	[195]
Pb (II)	Synthetic wastewater	Biosorption onto exopolysaccharides, extracted from bacterial strain coded TS7	277.54	[196]
Au	Au-containing industrial wastewater	Direct biosorption onto exopolysaccharide (Cyanothecae sp., <i>Nostoc</i> sp., <i>Rhodospseudomonas palustris</i> , <i>Rhodobacter sphaeroides</i>) microorganisms	Cyanothecae (318), <i>Nostoc</i> (64), <i>R. palustris</i> (80), <i>R. sphaeroides</i> (45)	[197]
Cu (II), Ni (II)	Synthetic wastewater	Bioaccumulation inside the cells (<i>Candida</i> sp.)	Cu (36,9), Ni (46.8)	[198]
Pb (II)	$\text{Pb}(\text{NO}_3)_2$ solution	Adsorption/accumulation by exopolysaccharide and <i>Acinetobacter junii</i> Pb1	Loosely associated (1071) and bound (321.5) to exopolysaccharide, whole cells (165)	[194]
Cd, Cu, Mn, Zn	Synthetic wastewater	Direct bioaccumulation inside the cells (<i>Chlorella minutissima</i>)	33.7 (Zn), 21.2 (Mn), 35.4 (Cd), 3.3 (Cu)	[199]
As (III), Fe (II)	Synthetic wastewater	$\text{Fe (II)} + \text{O}_2 \rightarrow \text{Fe (III)}_{(\text{aq})} \rightarrow \text{jarosite: ((K, Na, NH}_4\text{) Fe}_3\text{(SO}_4\text{)}_2\text{(OH)}_6\text{)}$, As (III) _(aq) + biogenic jarosite \rightarrow As-Jarosite	99.5	[200]
Pt, Pd, Rh	Spent automotive catalysts	Glycine converted to NaCN $2\text{Pt} + 8\text{NaCN} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Na}_2\text{(Pt (CN)}_4\text{)} + 4\text{NaOH}$ (<i>Chromobacterium violaceum</i>)	92.1 (Pt), 99.5 (Pd), 96.5 (Rh)	[201]

essential. Hybrid ion exchange nanotechnology (HIX-Nano) produces a valuable nutrient solution after removing phosphorus from contaminated media. Using the design of experiments approach, Ownby et al. [202] studied the phosphorus desorption from a commercial HIX-Nano resin hybridized with Fe_2O_3 nanoparticles. A mixture solution of $\text{KOH}/\text{K}_2\text{SO}_4$ and recycled alkaline NH_4OH and tap water was employed instead of synthetic acid. They used KOH and H_2SO_4 solutions as control samples. The efficiency of 75 % resulted for phosphorus recovery utilizing a mixture solution of NH_4OH and tap water. The hybrid of HIX-Nano resin/ Fe_2O_3 nanoparticles showed high stability after five consecutive adsorption and disposal process.

Pengyi Yuan and Younggy Kim investigated phosphorus recovery from a local wastewater treatment plant by microbial electrolysis cells. Fig. 5 shows the schematic diagram of the microbial electrolysis cells constructed of stainless steel foil cathode and an exoelectrogenic bacteria supported on a graphite fiber brush in the role of bioanode [206]. They evaluated different cathode arrangements in a laboratory-scale cell for optimal precipitation of struvite crystals ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$). Under an electric current of 2 A/m^2 , a thick layer of struvite is deposited on the cathode surface. The fabricated microbial cell achieved 96 % phosphorus recovery during 7 days of operation.

Okano et al. [207] used the amorphous calcium silicate hydrates (A-CSHs) to recover phosphorus from aqueous solutions. Fig. 6 shows the

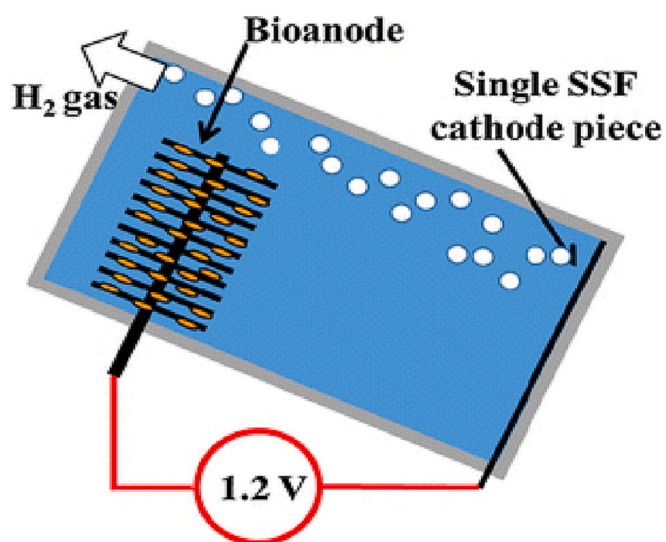


Fig. 5. Schematic of microbial electrolysis cells fabricated with a stainless steel foil cathode and a bioanode. A graphite fiber brush supporting the exoelectrogenic bacteria played the role of bioanode. Reprinted from Ref. [206].

mechanism of phosphorus recovery with calcium silicate hydrates. The 69 % phosphorus removal from an anaerobic sludge digestion liquor including $89 \text{ mg PO}_4^{3-}/\text{L}$ by 1.5 g/L A-CSHs reveal the high efficiency of the developed procedure. The phosphorus removal was improved up to 82 % following the A-CSHs washing with deionized water by which free calcium hydroxides are omitted from A-CSHs. Moreover, sedimentation, filtering, and dewatering for eliminated phosphorus by A-CSHs is done better than the sample obtained by CaCl_2 and Ca(OH)_2 .

5.3. Recovery and reuse of ammonia and nitrogen from wastewater

Demand for phosphorus and nitrogen has increased due to the development of food production. The Haber-Bosch procedure produces fertilizers based on nitrogen through the industrial stabilization of nitrogen to ammonia. The wastewater treatment is a high-energy consumption process in which nitrogen is mainly converted to N_2 gas that is lost to the atmosphere. Several technologies are available today for recycling nitrogen from wastewater [208–211], Fig. 7: (1) direct nitrogen recovery from wastewater or rejected water originates from the dewatering of digested sludge, 2) concentrating nitrogen content in wastewater or rejected water, 3) treatment of sewage sludge and urine, 4) nitrogen recovery in form of biomass [212].

Nitrogen-containing pollutants enter the environment due to the combustion of solid fuels from sludge. He and coworkers [213] designed a hydrothermal-based deamination and deaeration system to recover and reuse nitrogen from sewage sludge (Fig. 8). Four hydrothermal procedures were applied for amine elimination. At a temperature below $300 \text{ }^\circ\text{C}$ and a pressure of 9.3 MPa (inorganic nitrogen, labile protein nitrogen), and by increasing the temperature and pressure to $340 \text{ }^\circ\text{C}$ and 15.5 MPa , deamination processes were performed. Protein-nitrogen deamination occurred significantly at $380 \text{ }^\circ\text{C}$ and 22 MPa , which resulted in the removal of $\text{NH}_4^+\text{-N}$ (7980 mg/L) and nitrogen (76.9 %) from the sewage sludge. Deamination of stable protein, pyridine, and pyrrole was accelerated by adding calcium oxide for fracturing and catalytic hydrolysis processes, and the conversion of quaternary protein-nitrogen to nitrile and pyridine was desired. In this process, the total nitrogen removal efficiency and recovery rate reached 86 % and 62 %, respectively. In addition, ammonium sulfate was used to remove and recover ammonia from the liquid portion.

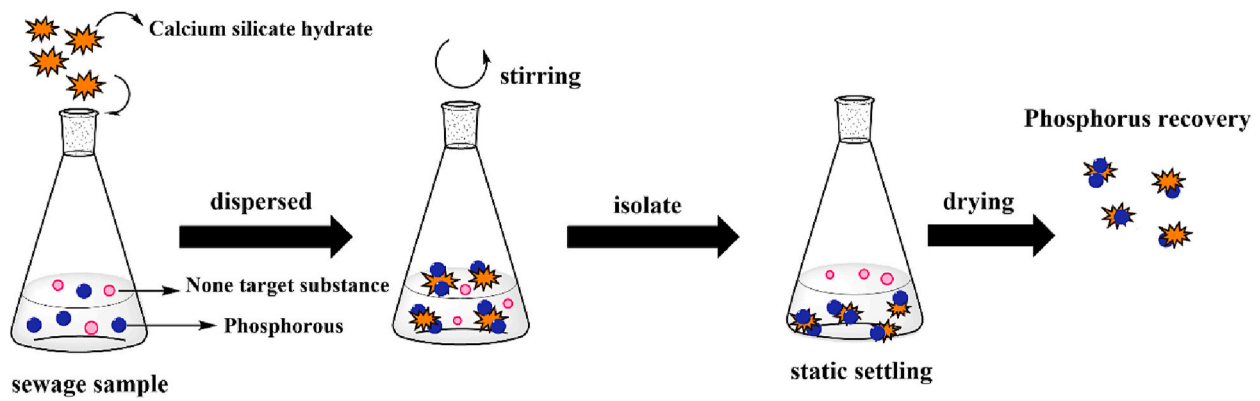


Fig. 6. Process of phosphorus removal from contaminated solutions utilizing amorphous calcium silicate hydrates. The recovery is performed via a three-step procedure. This method benefits from cheapness, abundance and easy access to amorphous calcium silicate hydrates. High performance recovery of phosphorus from synthetic model liquor (s-ASDL), anaerobic sludge digestion liquor (ASDL) containing 89 mg $\text{PO}_4^{3-}/\text{L}$, was performed by the amorphous calcium silicate hydrates (A-CSHs). After 20 min of stirring, CSH hydrates have removed 73 % and 69 % of phosphorus from s-ASDL and ASDL, respectively. However, under the same experimental conditions, particles of lightweight concrete containing A-CSHs were able to eliminate only 6 % and 10 % of phosphorus from s-ASDL and ASDL, respectively.

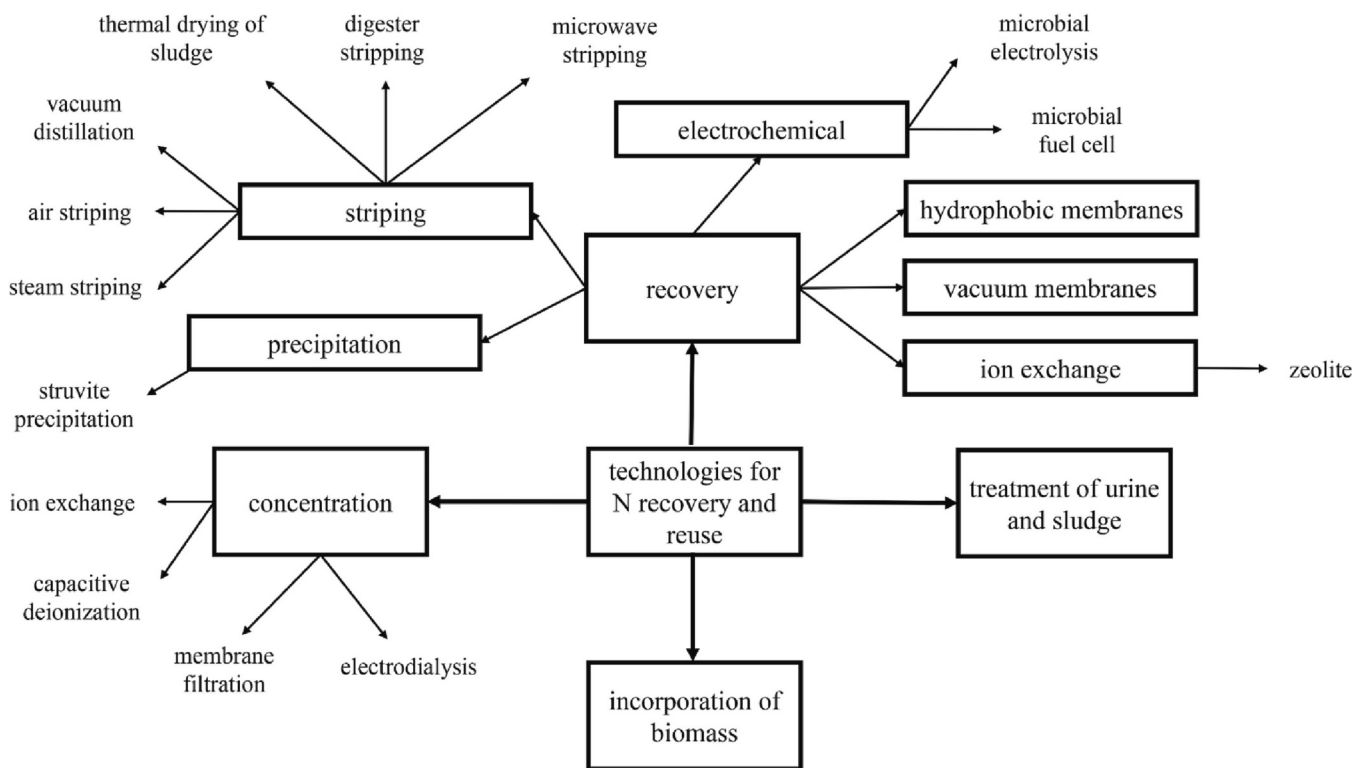


Fig. 7. Outline of strategies with related techniques to recover and reuse nitrogen. Categorized technologies used to recover and reuse nitrogen from wastewater. 1) Recovering nitrogen directly from wastewater or reject water originating from the dewatering of digested sludge, 2) recovery through nitrogen concentrating in wastewater, 3) purification of sewage sludge and urine, 4) incorporating nitrogen in biomass. Reprinted from Ref. [212].

6. Technologies for resource recovery

Recovering valuable resources is of great importance for completing the sustainability circle of new urban societies. Accordingly, current studies focus on recovering nutrients, organic carbon, precious metals, and energy from various resources [214,215]. Developed technologies for substances and energy recovery are based on biorefinery, biological treatment, thermal-chemical process, biosorption, and hydrothermal conversion. Researchers have focused on the recovery of organic constituents, mainly carbon, heat, and nutrients from a variety of wastes

and effluents.

The combustion of fossil fuels leads to the production of flue gas that is rich in sulfur and nitrogen oxides. The harmful effects of these gases, which the most obvious of them being global warming due to the greenhouse effect and acid rains, have made it necessary to recover and prevent them from entering the atmosphere [216]. For example, the SO_x or NO_x pollutants are traditionally removed from flue gas via liquid-based adsorbent through a wet scrubbing process. However, investigation indicated that heterogeneous adsorbents performance is better and in term of recycling and economic efficiency are superior to liquid-based

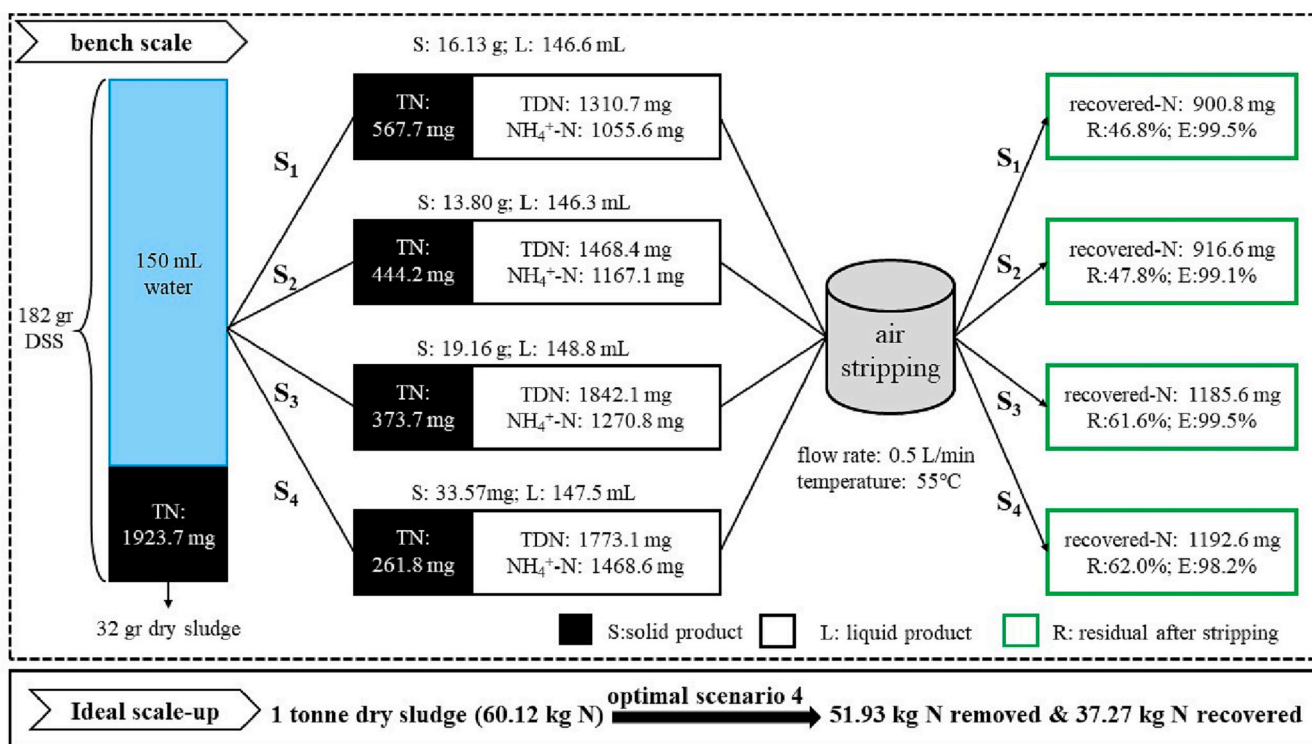


Fig. 8. Nitrogen recovery amount and ammonium removal capability under four typical techniques. Hydrothermal technique was applied for amine elimination. At a temperature below 300 °C and a pressure of 9.3 MPa (inorganic nitrogen, labile protein nitrogen), and by increasing the temperature and pressure to 340 °C and 15.5 MPa, deamination processes were performed. Protein-nitrogen deamination occurred significantly at 380 °C and 22 MPa, which resulted in the removal of NH₄⁺-N (7980 mg/L) and nitrogen (76.9 %) from the sewage sludge. Deamination of stable protein, pyridine, and pyrrole was accelerated by adding calcium oxide for fracturing and catalytic hydrolysis processes, and the conversion of quaternary protein-nitrogen to nitrile and pyridine was desired. The ammonia was eliminated and recovered from the liquid portion as ammonium sulfate in an efficient air removal process. In this process, the total nitrogen removal efficiency and recovery rate reached 86 % and 62 %, respectively. (S1: Scenario 1 (340 °C, 15.5 MPa), S2: Scenario 1 (380 °C, 22.0 MPa), S3: Scenario 3 (380 °C, 22.0 MPa, Ca/C = 0.05), S4: Scenario 4 (380 °C, 22.0 MPa, Ca/C = 0.2), R: Recovery rate of N as (NH₄)₂SO₄, E: NH₄⁺-N removal efficiency after 24 h). Reprinted from Ref. [213] with permission from Environmental science & technology.

adsorbents.

Thermal energy recovery from municipal wastewater, wastewater treatment plants, and even domestic water can be done with the help of a thermal converter with a heat pump [217]. Not only heat but also nutrients and valuable materials can be recovered from industrial and agricultural wastewater and even sewage. For example, phosphorus is converted to struvite and recovered. Extracting valuable materials such as methane containing biogas and ethanol from remaining wastes is an effective way to recover renewable energy. Conversion of various waste components into valuable products is a sustainable solution in resumption of the renewable energy. Phosphorus extraction from sewage sludge, food, animal and agricultural waste and recovery of precious metals and transition metals from mining waste, municipal and industrial waste, and electronic waste such as silver and gold recovery from printed circular boards are examples of the valued recourse recovery [217].

Among these fields, nanobiocatalysts play an important role in energy recovery from oils. Biodiesel is well-known as the most essential form of recovered valuable energy resource. Biodiesel is a biodegradable and renewable fuel consisting a mixture of long-chain fatty acid esters. Commonly, biodiesel is produced through the chemical or enzymatic transesterification of vegetable oils, animal fats, or recycled greases in the presence of monohydric alcohols. Diverse technologies are carried out to convert the oil into biodiesel, such as pyrolysis, microemulsion, and transesterification. Among the various traditional methodologies for resource recovery aimed at biodiesel production, transesterification has appeared as one of the best methods because the physicochemical properties of the obtained biodiesel are comparable with petroleum

diesel and do not require any adjustment before use in vehicle engines. The transesterification process could be improved by utilizing distinctive types of catalysts. Considering the catalyst type, transesterification may be categorized into five classes, including acid, alkaline, lipase, transition metal compound, and silicates catalyzed transesterification [218,219]. Transesterification is a 3-step process that calls for a temperature around 60 to 70° centigrade related to the activation/boiling point of the used alcohol. This process is irreversible and requires a catalyst to enhance the efficacy of the reaction. Typically, the starting materials of this reaction are triglycerides (oils and fat) and alcohol. As aforementioned, it is a multi-step reaction. Diglycerides are first formed by the reaction of methanol with triglycerides. Then, the as produced diglycerides react with the residual methanol to form monoglyceride. Finally, glycerol is formed from the reaction of monoglycerides with methanol. Fig. 9 shows a summary of the transesterification process. Generally, primary catalysts are used in this process, and the reactants are heated in the presence of a catalyst [220,221].

7. Limitations

Recovering valuable resources from waste faces various drawbacks, including uneconomic raw materials, several long steps, and low conversion rates. The scientific community is always looking for new ideas to develop a process to address these issues. In this regard, the enzymatic method has been considered due to the higher conversion rate, lack of soap formation in the reaction chamber and the pervasive recovery/purity properties of the synthesized products. The use of lipase enzymes also makes it possible to work with a wide range of raw materials. For

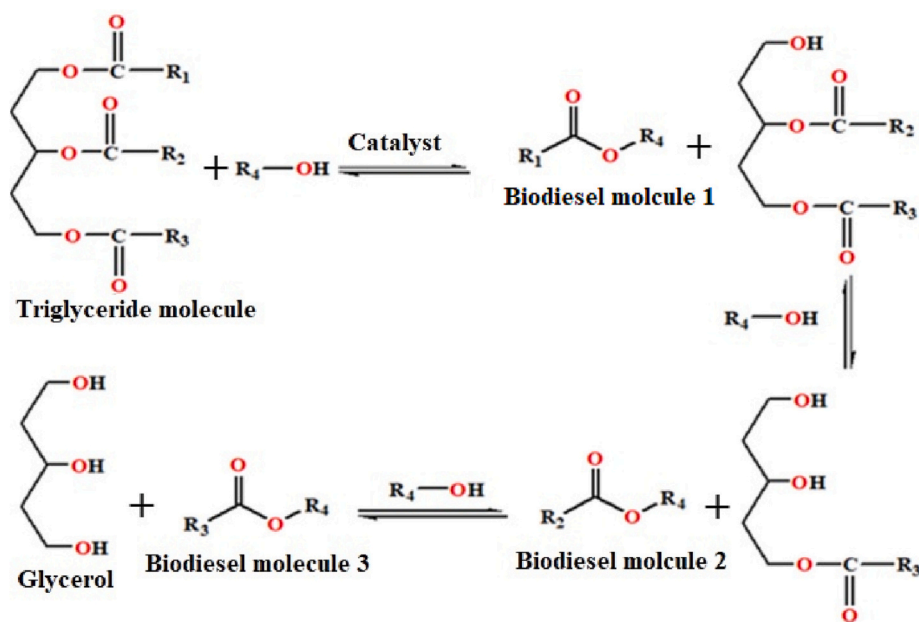


Fig. 9. Three-step transesterification process. The process starts with diglycerides production by the reaction of methanol and triglycerides. The produced diglycerides react with remaining methanol for monoglycerides formation. Finally, the monoglycerides react with excess methanol to form glycerol production as final product. Basic catalysts are required for the enhancement of the process efficiency. The application of nanobiocatalysts has improved the transesterification efficiency. Reprinted from Ref. [222].

example, in the usual methods used when working with animal fats and frying oils, the problems of free fatty acids and moisture must be overcome. However, the lipase enzyme can be effective even in these problematic cases [223]. Despite the mentioned advantages, the use of lipase enzyme also has disadvantages. We can point to the low stability, low recovery rate, and low effectiveness of free enzymes at high temperatures and pH, which limit the industrial application of this process [224,225].

To overcome the problems of using lipase as a catalyst in the transesterification process, the application of lipase stabilization techniques on solid substrates has been widely used in the production of biodiesel in recent years. In this regard, the application of nanotechnology in the development of lipase stabilization substrates has achieved remarkable success. These nano-substrates provide a suitable microenvironment for enzyme stabilization by introducing nano-dimension pores and a larger active surface available for enzyme stabilization. In addition,

nanoparticles support fewer structural constraints and more brown motions, which improves enzymatic performance. Various nanobiocatalysts with different nanoparticle sizes, shapes, and compositions have been introduced for biodiesel production. The capability of enzyme recovery and reuse, along with reducing the associated costs, has made nanobiocatalysts a promising solution in the production of biodiesel using enzymatic reactions. Fig. 10 provides an overview of recent developments and conventional methods in biodiesel production.

Disadvantages like the low stability, low recovery rate, and low effectiveness of free enzymes at high temperatures and pH limit the industrial application of enzyme-based catalysts. The nanobiocatalysts have shown well that they are capable of solving these restrictions and successfully catalyze many reactions.

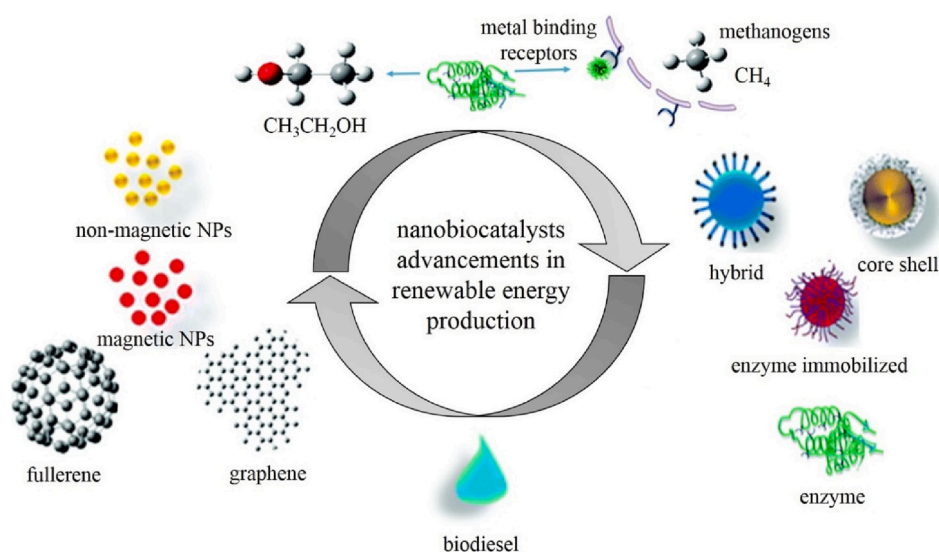


Fig. 10. Renewable energy plays an important role in the field of resource recovery. Various nanobiocatalysts have been developed for the production of biodiesels as an on demand renewable energy. The capability of enzyme recovery and reuse, along with reducing the associated costs, are attractive benefits that nanobiocatalysts can afford. This schematic represents recent developments and conventional methods in biodiesel production. Reprinted from Ref. [226].

8. Economic aspects

To cope with the economic crisis and the scarcity of natural resources, the international community must move toward replacing the linear economy with a circular economy [227,228]. Unlike linear economics, which is based on production, consumption, and disposal, circular economics emphasizes use and recycling. Given the unprecedented growth of the world's population, sustainable growth based on the circular economy model must be considered and implemented to ensure the provision of food, water, and energy for future generations [229,230]. More efficient management of raw materials and minimization of waste is very important. A circular economy can guarantee less waste generation and a sustainable way of producing chemicals and energy.

Switching to biodiesel is an economically feasible and sustainable option to replace petroleum-based diesel. The ability to use biodiesel, produced from renewable and recyclable sources, as fuel for existing diesel engines without further modification is an additional advantage [231]. Fungal biosystems and oily yeasts utilize organic waste as an energy source for lipid bioaccumulation [232]. *Lipomyces* sp., *Rhodotorula* sp., and *Rhodospiridium* sp. are known strains of yeasts that can produce intracellular lipids. In fact, 70 % of the biomass of these yeast strains is composed of lipids, which makes it possible to use them as a source of biodiesel production [232]. Used cooking oil, wheat straw, rice husk, and carbon from glycerol can be utilized as resources for fat production by oily fungi [115,233]. The esterification process is the next major step for biodiesel production, where the biomacromolecule-based nanobiocatalysts plays crucial economic role.

It is important to note that free enzymes are readily inactivated in the presence of short-chain alcohols, especially methanol, which is used in the esterification process at high temperatures and pHs [79]. Meanwhile, the stabilization of the enzyme on the surface of nanoparticles and the production of nanobiocatalysts increase the resilience and maintain the function of the enzyme against environmental conditions by creating a suitable microenvironment. On the other hand, most of the nanobiocatalysts utilized in the transesterification process have the capability of reuse up to five times, unless the enzyme activity is significantly reduced. Hence, nanobiocatalysts can help reduce the cost of the biodiesel production process. In this regard, lipase stabilization on the surface of nanoparticles and the production of effective nanobiocatalysts for the transesterification process is vital for the economics of the biodiesel production process.

Currently, the immobilization of bio-macromolecules onto different types of nanomaterials has been widely applied to economically improve the overall process by making nanobiocatalysts reusable many times [234–236]. The immobilized bio-macromolecules is found in numerous implementations in chemical industries, pharmaceutical, food, and biofuels [234,237]. For the resource recovery approach to be implemented with the help of nano-biocatalysts, long-term stability, the possibility of recovery as well as the possibility of commercialization of nano-biocatalysts must be considered. Cooperation between governments, scientists, and companies in developing and developed countries is needed according to a coordinated framework and strategy to ensure a global sustainable market for the usage of resource recovery technologies. Strict legal frameworks should also be provided for wastewater and waste disposal and resource recovery to diminish environmental pollution and improve resource recovery and reuse [238].

9. Conclusion

Nanobiocatalysts are a new generation of catalysts that benefit from outstanding properties of both biocatalysts and nanomaterials. The combination of nanomaterials with biocatalysts is considered an efficient engineering strategy to overcome the disadvantages like the low stability, low recovery rate, and low effectiveness of free enzymes at high temperatures and pHs. On the other hand, the prominent

nanoproperties in nanobiocatalysts provide a wide active surface area, long-term stability, resistance, increased catalytic activity, greater selectivity, easier operating conditions, and cost-effectiveness for the biocatalysts. Integrating magnetic nanomaterials with nanocatalysts has made nanobiocatalysts recoverable and reusable. Therefore, the high operating costs associated with the production of enzymes and the synthesis of nanocarriers are offset and bring economic benefits.

The application of technologies based on nanobiocatalysts is still in the early stages of entering the valuable resource recovery industry. The mechanisms of nanobiocatalysts action and their related properties are not yet well understood. Nanobiocatalysts must have four key characteristics to successfully enter the field of industrial processes: (i) high stability in harsh environments, including organic solvents and changes in temperature and pH, (ii) the ability to recover and reuse biocatalysts in successive reaction cycles, which has great importance from an economical and technical point of view, (iii) maintaining the activity and efficiency of the enzyme at the desired level of process conditions, as well as reducing enzyme leakage, (iv) high-yield for large-scale processes.

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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