



Review article

Silica nanobiocatalyst: Advancements toward sustainable and innovative applications

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ABSTRACT

Nanobiocatalyst is a useful technological development that brings together modern nanotechnology and biotechnology and offers benefits for enhancing the activity, stability, and performance of enzymes in bio-processing applications. Nanosupports used in nanocatalysts have a number of advantages over conventional materials, including a robust framework, tunable morphology, increased surface area, excellent pore geometry, inherent properties, and distinctive optical properties for the supporting matrix. Nanobiocatalysts based on silica have been used in drug delivery, optical imaging, pollution control and other catalytic processes. In this review we trace the development of silica-based nano-bio catalysts as a supporting matrix, discussing their structure-property relationships and discuss molecular-level interactions between enzymes and surfaces. The influence of parameters such as pore size, morphology, and surface modifications on immobilisation efficiency and resulting activity is also examined. Additionally, a summary and significant advancements of silica-based nano biocatalysts with potential future applications in the production of biofuel and bioremediation is provided. Overall, the review identifies nano-silica biocatalysts as a promising support and suggests future directions and challenges.

1. Introduction

Enzymes are biocatalysts that increase reaction rates without getting consumed [1]. However, due to certain limitations such as low stability, non-recyclability, and high cost, their usage at the industrial level is challenged [2]. To overcome these challenges, immobilisation provides numerous benefits such as reusability, stability, and catalytic proficiency efficiency under different environmental conditions [1,3–6]. Enzyme immobilisation requires confinement or localization of an enzyme/biocatalyst in a certain region of defined space with retention of catalytic activity under optimized parameter conditions [7]. An essential aspect of enzyme immobilisation is the development of appropriate nano-supports. Nano-based supports have numerous advantages over

traditional supports due to improved enzymatic properties such as catalytic stability, higher enzyme loading, performance, and repeatability [8,9].

Moreover, the nature and selection of the type of nano support are crucial in determining enzymatic activity, specificity, and stability [10]. Various supports exist, ranging from porous, nonporous, rigid, flexible, membrane-based, macro-porous, or nanostructured. However, immobilizing an enzyme on different nano-support types can enable a range of industrial and medical applications [11]. Nano-enabled biocatalysts are designed by synergetic integration of selected enzymes on tailored nanomaterials with higher enzyme loading capacity, superior mass transfer efficiency, and resistance to temperature and pH changes [12–15]. Numerous investigations have been conducted to explore

Abbreviations: APTES, 3-aminopropyltriethoxysilane; BJH, Barrett-Joyner-Halenda; BET, Brunauer-Emmett-Teller; CPTES, Chloropropyltriethoxysilane; CLEAs, Crosslinked enzyme aggregates; HMMS, Hierarchical ordered mesocellular mesoporous silica; MSNs, Mesoporous silica nanoparticles; MCM series, Mobil Composition of Matter; MCM-41, Mobil Composition of Matter No. 41; MCF, Mesoporous cellular foams; MPS, Mesoporous silicates; MNPs, Magnetic Nanoparticles; NPs, Nanoparticles; OMMs, Ordered mesoporous material; RH, Rice husk; RHA, Rice husk ash; SBA, Santa Barbara Amorphous; TMOS, Tetramethoxysilane; TEOS, Tetraethoxysilane; US FDA, The United States Food and Drug Administration.

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organic, inorganic, and polymeric nanocarriers such as graphene, mesoporous silica, carbon-nano tubes, liposomes, and nanostructured metal oxides frameworks to host enzymes [16]. In addition, different research groups are exploring more economical and efficient alternatives to current supports [3,15,17] due to the high cost involved in developing these supports for large-scale industrial applications.

Silica-based nano supports have shown advantages over other nanomaterials for enzyme immobilisation as they are robust, inert, cost-effective, and straightforward [8,18]. The surface properties of silica nanoparticles can be modified easily with different functional groups [19–21]. The surface-modified silica NPs thus find applications in biomolecule detection and separation, drug delivery, and as biocompatible pharmaceutical additives [22]. Moreover, silica is "Generally Recognized as Safe" by the United States Food and Drug Administration (FDA). Silica nanoparticles in the form of Cornell dots (C dots) received FDA approval for stage I human clinical trial for targeted molecular imaging [23,24]. It was reported that mesoporous silica nanoparticles (MSNs) exhibit a three-stage degradation behaviour in simulated body fluids [25], suggesting that MSNs might be degraded after administration, which is favourable for cargo release. MSNs may be used efficiently in various applications, including optoelectronic devices, sensors, pharmaceuticals, and environmentally sensitive pursuits, due to their excellent adsorption properties [18]. Enzyme immobilisation on mesoporous silica has become more critical because of its potential in biomedical applications. Mobil Corporation laboratories have developed MSNs with a highly ordered hexagonal array of one-dimensional pores, named Mobil Composition of Matter No. 41 (MCM-41) [18,26].

MSNs are promising and exhibit unique properties for enzyme immobilisation due to their larger surface area to volume ratio, ease of nanomaterial fabrication, and surface functionalization [8,27]. Their nano-size, architecture, morphology control, and overall pore geometry [28] allow a greater coupling of the enzyme for catalysis [18,29] as a drug carrier [30] and sensors [31]. There are numerous associated benefits with MSNs, such as increased enzyme stability, selectivity, and reusability [32]. MSNs exhibit high loading capacity for therapeutic agents and controlled release properties if modified with stimuli-responsive groups, polymers, or proteins [33], thus improving overall enzyme stability, catalytic activity, specificity, and greater resistance to extreme environmental conditions [34–36]. The present review collates essential features of various biocatalysts immobilized on nano-silica platforms. This includes the mode and techniques of immobilisation, surface modifications, and parameters related to free, immobilised enzyme activity, reusability and stability. Appropriate selection of nano-platform supports, their advantages and applications in biodiesel production, biotransformation and bioremediation are briefly outlined. In addition, structure-property relationship of immobilised enzymes has also been reviewed in detail.

2. Natural feedstocks as a source of silica

In nature, numerous forms of minerals exist in different forms that are assimilated by the biota [37]. Silicon is the second most abundant element in the Earth's crust. Silica is present widely in nature in several forms, such as R-quartz, opaline silica, and amorphous silica [38,39]. Moreover, the existence of silica in most biological systems is well established [40,41]. Accumulation of silicon by diatoms and other living creatures such as silico-flagellates, radiolarians, some plants, bacteria, fungi, sponges, and molluscs, is well known [42]. Specifically, silica bio-mineralization in diatoms, single-celled photosynthetic microalgae belonging to the family Bacillariophyceae is a matter of ongoing investigation since it produces numerous hierarchical nanostructures used in some industrial applications [43–48].

On the other hand, silica has been successfully extracted from different agricultural materials like rice husk [49,50], wheat husk [51], and corn cob [52]. Rice husk ash (RHA) and corn cob consist of a significant amount of silicon and serve as another example of

bio-mineralization of silica in their cell wall [53–55]. Therefore, their composition and ability to produce large amounts of biomass economically make them an ideal candidate for silica extraction [56,57]. The extraction of silica from agricultural waste typically involves alkaline extraction followed by an acid neutralization process [58]. Initially, metallic impurities within the waste are removed through acid refluxing at temperatures reaching up to 120 °C [50]. Subsequently, the activated ash undergoes treatment with sodium hydroxide (NaOH) solution to yield sodium silicate [59]. Finally, the addition of hydrochloric acid (HCl) solution to the sodium silicate results in the formation of pure silica in gel form. In the literature, numerous strategies for the recovery of silica from agriculture waste and their conversion into nano-silica are well reported [55,60,61]. The following section briefly discusses synthesis approaches for silica and MSNs.

2.1. Inorganic synthesis strategy of nano-silica and MSNs

Nano-silica and MSNs offer several advantages [31] for use as chemical sensors, agents, or carriers for drug delivery due to their chemical inertness and stability [31,62]. Therefore, several processes, such as sol-gel, hydrothermal, aerogel-based methods, microwave, and templating-based synthesis, are adopted to obtain silica nano-variants [18]. However, The Stober method [63], based on the sol-gel process, is widely assumed to synthesize monodispersed silica nanoparticles.

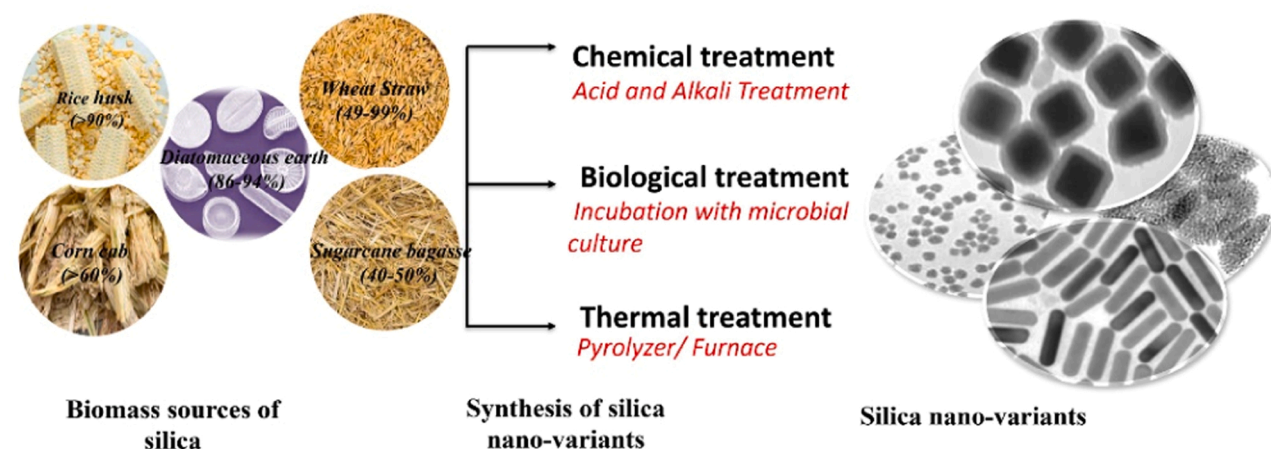
Nano and micro-sized silica particles can be synthesized by a template-driven process using various kinds of surfactants that act as structure-directing agents [64]. The morphology, particle, and pore size of the synthesized MSNs are primarily dependent on the surfactants' template properties. Parameters such as temperature, pH, and silica precursor are the determining factors for producing variants of MSNs [31]. For instance, thin films, fibers, spheres, and bulk forms, such as the SBA [65] and MCM series [66], are common variants of MSNs.

Generally, a silica precursor, a catalyst for silica polymerization, a surfactant template, and a solvent are prerequisites for synthesizing mesoporous surfactant-templated silicates [18]. The following processes can synthesize ordered mesoporous materials (i) Folded sheet mechanism. First, organic compounds are inserted between the layered silicates, followed by heating or ion exchange. This, in turn, causes the silica to get condensed into a three-dimensional network of silicates [67] (ii) Liquid Crystal Templating method, wherein the surfactants are initially formed into micelles followed by the polymerization of the inorganic silicate species [68] and (iii) lastly, in the evaporation-induced self-assembly procedure, the concentration of the surfactant solution is increased by slowly evaporating the solvent, to generate enough micelles forcing the silicate to precipitate and create the mesoporous material [69]. Finally, the template is removed through calcination, and the porous structure with exceptional structural and biomedical properties is generated (Fig. 1) [33,70]. The detailed hydrolysis and condensation reaction mechanisms under acidic and alkaline conditions are adequately described in the literature [8,18,71]. The following section discusses the advantages of silica nano variants as a supporting matrix and strategies available for enzyme immobilisation.

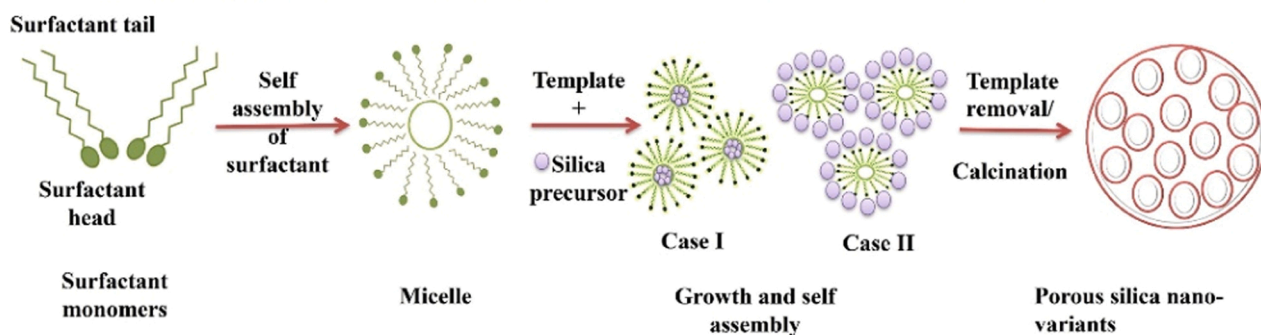
3. Enzyme-enabled nano-silica support

For the preparation of an efficient, cost-effective nano-enzyme immobilized system enzymes and related support need to facilitate certain conditions [72]. For example, (i) large surface to volume ratio for increased enzyme loading, (ii) thermal and chemical stability to withstand reactions parameters, (iii) bio-compatibility and ease of functionality to produce an efficient enzyme immobilized system, (iv) reusability of the immobilized system (v) economic viability and environmental sustainability [12]. Therefore, an efficient, cost-effective system with the above characteristics can improve enzyme activity, stability, and reusability.

In terms of enzyme immobilisation, inorganic porous materials with



(a). Synthesis of silica nanoparticles from different silica biomass source



(b). Diagrammatic representation of formation of porous silica nanoparticles

Fig. 1. Diagrammatic representation of formation of silica nanoparticles.

large volumes and specific surface areas are promising support. For example, researchers have developed materials based on silica, such as MCM-41 and SBA-15; MCF possesses smaller pore sizes and added advantages as a suitable support for enzyme immobilisation [73].

3.1. Modes of enzyme immobilisation

Enzyme immobilisation is characterized by four classes based on the interaction between the support and enzymes. These are namely (i) adsorption, (ii) entrapment (iii) covalent bonding, and (iv) cross-linking [74,75]. Each method has its advantages and limitations. Adsorption is the simplest, economical, environmentally benign, and effective mode used to immobilize enzymes [8,72]. Physical immobilisation (adsorption) is accomplished by direct contact between adsorbate and adsorbent at the optimal temperature [76,77] without any chemical compounds [78,79]. In adsorption, weak interaction such as hydrogen bonding, hydrophobic interactions, Van der Waals forces between enzyme and support makes an unstable complex. In contrast, the entrapment mode of immobilisation involves the physical confinement or caging of enzymes [72] within the organic or inorganic polymeric network where enzymes cannot seepage. However, movement of substrate or product is allowed [80].

In contrast, in covalent immobilisation, enzymes are covalently attached to the substrate with the help of elements offering active groups that can be bonded to the enzyme [81] and biocompatible material like polydopamine or glutaraldehyde [13]. Therefore, it is a robust, practical, and durable technique. However, it is expensive and sometimes may lower the enzyme performance.

Another technique, crosslinking, involves the formation of

intermolecular cross-linkages among enzyme molecules, achieved through irreversible covalent bonds [82]. This process utilizes bi- or multifunctional reagent as linkers to connect enzyme molecules into a three-dimensional cross-linked aggregate leading to formation of cross-linked enzyme aggregate (CLEAs) [83–87]. As covalent bond formation also occurs during crosslinking, it proves to be a robust immobilisation process with advancement in stability and reusability [88]. Cross-linked enzyme aggregate (CLEA) technology is recognized as a carrier-free immobilisation method known for its simplicity, robustness, and ability to co-immobilize multiple enzymes [89–91]. While CLEAs demonstrate high catalyst productivity and stability, certain limitations hinder its widespread application despite being utilized with various enzymes [92,93]. CLEAs are an innovative process for immobilizing enzymes on large porous silica structures [87] like HMMS [94] and MCFs [95,96].

Different strategies for enzyme immobilisation on nano-supports such as adsorption [101,102], covalent attachment [103,104], and crosslinking [97] were compared and examined to demonstrate the stability of immobilised enzymes further. For instance, Ivetić et al. (2014) compared the absorption yield using covalent bonding and physical adsorption by immobilisation of β -glucosidase on mesoporous based silica support with the micro-pore size of 29 nm. Compared to physical adsorption, covalent bonding using glutaraldehyde as a cross-linker and the silica support gave higher yields of bonded β -glucosidase along with higher activity and affinity. Biocatalyst obtained reserved around 70% of its initial activity up to ten cycles of reusability [98].

Covalent bonding creates robust and stable linkages between the support and enzyme [99], eradicating the activity loss caused due to

enzyme seepage from the carrier, and increasing the yield and activity. The upcoming section focuses on the silica nanoparticles/ silica-based nanocomposites (Si NPs/Si NCs) as a carrier for the immobilisation of various enzymes (Fig. 2). Several associated parameters, such as surface functionalization and modifications using multiple functional groups, strategies adopted for enzyme immobilisation, comparison between enzymatic activities of free and immobilised enzyme systems, and their recyclability and reusability studies are briefly discussed.

4. Nano-silica variants as a matrix for enzyme immobilisation

The essential characteristics of an immobilisation matrix or support are its structural and surface properties [100]. The large surface-to-volume ratio, bio functionality, and resistance to harsh reaction conditions favour enhanced loading of enzyme and the resulting activity [101]. Silica-based nano-supports with large silanol groups on their surface and well-ordered and tuneable pore structure make them practical supports for enzyme immobilisation [102]. As a nano-support for immobilisation of different enzymes and related enzymatic properties, the variant of silica is briefly summarised in Section 4.1.

4.1. Structural and morphological implications on enzyme immobilisation

The variants of silica nanoparticles with different structures and pore sizes have tremendous effects on the immobilised enzymes [15,103]. Enzyme adsorption is greatly affected by the relative size of the support material and pores relative to the enzyme size [104,105]. When compared to the size of enzymes, the ideal size of the support should be approximately 3–5 times [106–108]. The pore size of the support material is the most vital parameter for the efficient immobilisation of an enzyme [106]. For instance, to demonstrate the effects of different types

of structure and pore dimensions of the silica supports, cytochrome c was immobilised on silica one dimensional (MCM-41, SBA-15) and 3-dimensional (MCM-48) pore structures [109]. The study revealed increased enzyme loading for MCM-48 with reduced leaching and diffusion of the enzyme. Another study by Fan et al. (2003) showed that lysozyme adsorbed in conventional and rod-like SBA-15 [110,111] resulted in enhanced lysozyme adsorption in the case of SBA-15 compared to conventional supports.

Furthermore, a study demonstrated a direct influence and dependency of enzyme adsorption on the structurally distinct OMSs [112]. In another study by Singh et al. (2013), immobilisation of catalase within spherical hollow silica nanoparticles (HSNPs) with a pore size of about 50 nm was demonstrated. They compared enzyme activity between free enzymes with HSNPs entrapped enzymes under different parameters. The result indicated enhanced enzyme properties, including thermal stability and pH resistance compared to free enzyme. Thus, HSNPs entrapped enzyme displayed enhanced enzymatic activity, demonstrating the shielding of the enzyme against denaturation by the silica matrix of HSNPs [113]. A study by Luckarift et al. (2004) demonstrated that the biosilica synthesized using *in vitro* silicification reaction, with silicic acid and silaffin polypeptides sourced from diatoms, used in immobilisation of the enzyme butyrylcholinesterase. Around 90% of the initial activity of the free enzyme was present in the biosilica spheres after enzyme immobilisation [114]. In another study, synthesis of 'novel biohybrid' consisting of basil (*Ocimum basilicum*) seed and silica NPs were reported. The seeds acted as a template for silica NPs assembly and the enzyme invertase was immobilised on the biohybrid efficiently. The recyclability of up to 8 cycles with enzyme activity amounting to 82% was reported [115].

To better understand the immobilisation efficiency on variants of silica nanostructures, Ding et al. (2004) compared the enzyme loading

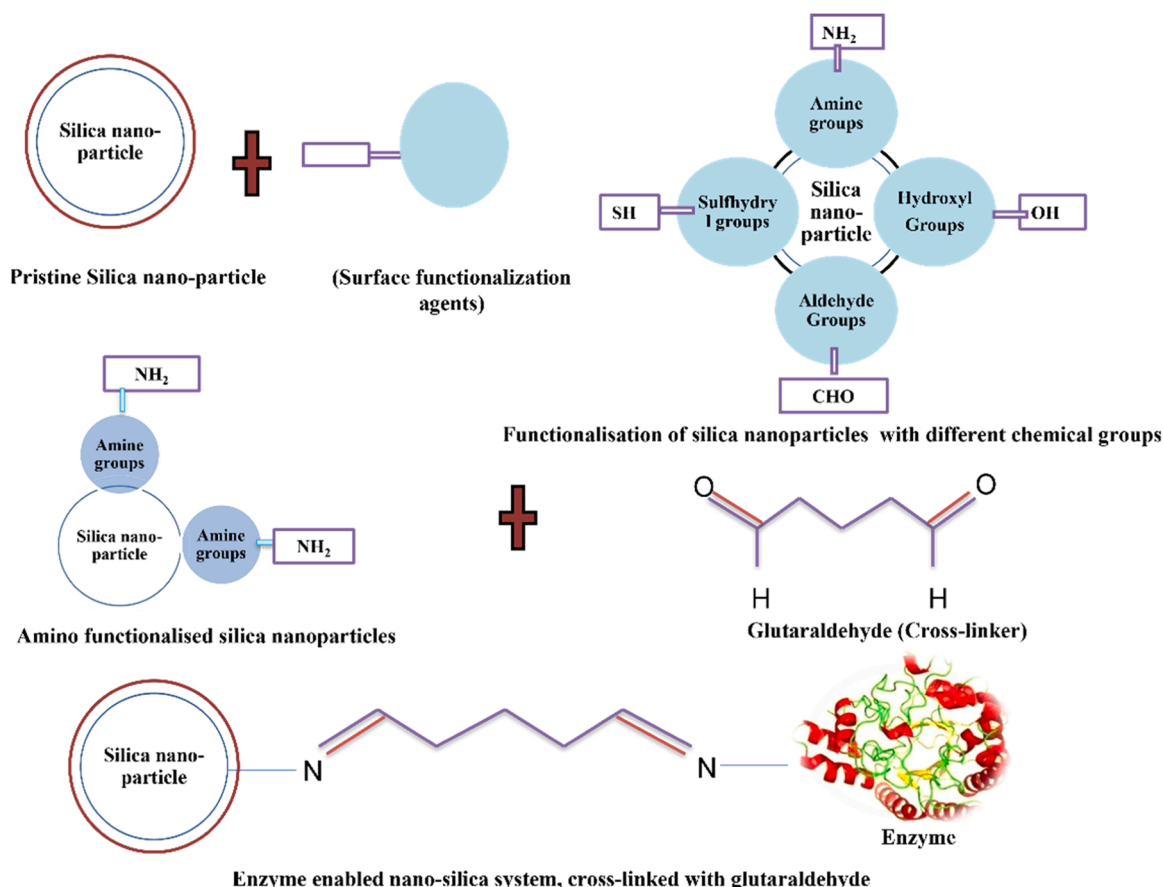


Fig. 2. Strategies for functionalisation of silica nanoparticles using different functional groups.

capacities between the commonly existing porous silica and mesoporous silica materials with synthesized porous silica nanotubes (NTPS). Increased loading capacity of NTPS (greater than 350 mg/g silica) was observed compared to other variants. The higher enzyme loading was investigated through a pore size analyser and BET. The result indicated enhanced loading efficiency in the case of NTPS due to hollow structure and large pore openings of NTPS, which were responsible for the smooth entry of most protein molecules and provided extra space for protein encapsulation. MPS pore channels were majorly responsible for the surface area as observed through BET. However, protein absorption in the pore channels was challenging, causing low protein loading and delay in adsorption equilibrium time [116].

To explore the influence of pore size on immobilisation efficiency, mesoporous materials called SBA-15 were synthesized by Gao, Wang et al. (2010). Diverse pore sizes among the five different support materials with pore-sizes of (6.8 nm, 9.1 nm, 13.2 nm, 15.6 nm, and 22.4 nm) were studied. *Candida rugosa* lipase (CRL) was crosslinked on the supports, and chitosan and glutaraldehyde were employed to prevent enzyme leaching. The support with a pore diameter of 15.6 nm was suitable with a high loading capacity of around 343.6 mg/g. The study showed that around 80.5% of immobilised CRL activity was obtained with recyclability up to 6 cycles in 48 hrs compared to free lipase [117]. In another study, Gustafsson et al. (2013) synthesized three particle sizes of mesoporous silica ranging from 1000 nm, 300 nm, and 40 nm, with a typical pore size of 9 nm for all three variants. Furthermore, the prepared silica variants were used as carriers to immobilise *Mucor miehei* and *Rhizopus oryzae* lipases. The variant with a 300 nm particle size was the most suitable support for both lipases in terms of their specific activity and enzyme immobilisation [118]. The authors concluded that mesoporous silica nanoparticles with a size of 300 nm were suitable for immobilising the enzyme. In the next section, surface modifications and their influence on immobilised enzymes are briefly discussed.

4.2. Influence of surface properties on enzyme immobilisation

Distinctive bio-functionality can be introduced to nanoparticles by modifying their surface properties [119,120]. Enzyme immobilisation on activated or surface modified supports enhances enzyme properties, thus, simplifying the reactor design [121–127]. Additionally, the abundance of surface hydroxyl groups on the surface of silica facilitates easy chemical surface modification, particularly advantageous for immobilizing lipases. Lipases, which often require interfacial activation for optimal catalytic activity, undergo a conformational change from an inactive "closed" form to an "open" active form upon adsorption at a hydrophobic/hydrophilic interface [128,129].

Approaches, such as the substitution of organic groups and inorganic elements, for instance, titanium, vanadium, aluminium etc., have been used to modify the surface properties of silica [15,127,134]. One such study was conducted by Vinu et al. (2004) to investigate the adsorption behaviour of lysozyme at different pH on SBA-15, MCM-41, and corresponding aluminium (Al) substituted materials. The higher loading efficiency of lysozyme was achieved from Al-modified silica variants compared to pure silica [127]. Due to many hydroxyl groups present on the silica surface, the bonding between enzyme and support becomes challenging. Thus, introducing organic functional groups such as amine, phenyl, alkyl and thiol on silica surfaces may improve the surface properties and help in surface modification. Yiu et al. (2001) prepared a series of functionalized SBA-15 materials with different functional groups and found a higher affinity of enzymes toward modified SBA-15 materials than pristine particles [130]. Therefore, reactive functional groups (NH₂ or CHO group) generate stable chemical bonds with enzymes [21,117,131]. Furthermore, cross linkers such as glutaraldehyde form stable and robust bonding with amino functionalised support through multi-step procedures or harsh conditions that are intervened during the process [21,117,131].

Porcine pancreas lipase (PPL) was immobilised on small porous

materials (MSC) and surface functionalized novel mesoporous silica supports (LPS-1 and LPS-2) modified by aldehyde group employing CPTES and APTES, respectively [100]. Furthermore, the enzymatic activity, properties of the MSC and modified LPS supports were compared. The overall enhanced enzymology properties and maximal activity of 76% were observed for LPS-2, followed by 69% of LPS-1 compared to 58% of MSC. The result depicted that LPS supports possess a cage-like larger porous structure that provided a suitable capacious microenvironment for immobilised enzymes [100]. Longer space arms of LPS-2 support also supported the substrate to access more quickly than LPS-1 as compared to the reported values of 62.8%, 59% [132], 66.7% [133] and 67.1% [134].

Bai, Li et al. (2006), [135] in one of their other studies, functionalised three novel nano-silica supports with aldehyde groups, namely NSD-1, NSD-2, and NSD-3. A covalent strategy was employed to immobilize PPL on modified NSD materials. The resulting immobilised NSD supports showed improved stability, reusability and higher K_M value than free PPL. The activities of NSD supports were compared, and a maximum of 118% activity was obtained in NSD-3, followed by 79 and 73% in NSD2 and NSD1, respectively [135]. Many reactive aldehyde groups were present on the surface of functionalised NSD-3. Therefore, the high loading of PPL was bound to its surface. Furthermore, they found that the long space-arms of NSD-3 own a monolayer molecular distribution and provide advanced accessibility of the active site of the immobilised enzyme to the substrate [135].

To demonstrate the advantage of surface modification, Jiang, Zhai et al. (2018) immobilised *Penicillin G acylase* (PGA) on silica nanoflowers, stabilized by a coating of polydopamine. The temperature, pH and operational stability of polydopamine coated PGA@nanoflowers, along with the enzymatic properties, improved significantly compared to both free and uncoated PGA@nanoflowers, depicting the advantages of polydopamine coating on their nano-support [136]. Low enzyme loading of mesoporous silica variants was observed by many researchers, possibly due to the absorption of enzymes on the external surface of the material with small pore size or enzyme leaching. Kang et al. (2007) observed the leaching of enzymes due to enormous pore size [105]. To overcome this issue of leaching associated with adsorbed enzyme and create stable confirmations between the support and enzyme, scientists suggested the usage of cross-linkers such as glutaraldehyde [137] and chitosan that creates a bridge unit and mesh-like structures to prevent leaching of enzymes [117].

5. Enzyme immobilisation on silica-magnetic nanocomposites

Magnetic nanoparticles (MNPs) are exceptional supports for enzyme immobilisation. Their low toxicity and easy separation by using magnets make them potential candidates as support materials [138]. The stability and biocompatibility of silica, when combined with MNPs, lead to the formation of desired nanocomposites [139]. The combination of two materials with their unique physical and chemical properties can enhance the overall properties of the final product. Therefore, researchers have synthesized silica-iron oxide composites with unique magnetic properties, which allow fast and rapid procedures for protein binding and separation [20,140,141].

Moreover, the composite can be recovered using a magnet due to the strong magnetic properties of iron, thus making the process more straightforward and economical [142]. The resulting nanocomposite finds application in various fields such as enzyme immobilisation [101, 143], targeted drug delivery [144], bioremediation [9], and separation or recovery of biochemical products [141,142]. MNPs were modified using TEOS and were surface functionalised by APTES. The resulting immobilised system depicted reusability up to 10 successive cycles with 51% residual activity [138]. In another study, Shao et al. (2015) immobilised lipase on synthesized mesoporous magnetic NPs under optimized conditions. The desired nanocomposite was further surface functionalized by grafting CPTS and 3APTS. In addition, enzyme

immobilisation was carried out using three different strategies covalent bonding, physical adsorption, and crosslinking. The results indicated that CPTS modified composite was the best candidate amongst all and displayed increased immobilisation efficiency of 96% along with higher stability and reusability up to ten cycles using covalent strategies [145].

Kalantari et al. (2012) synthesized superparamagnetic mesoporous silica nanocomposite, single (S1) and double-shell magnetite cluster cores of 130 nm. Lipase was immobilised on the synthesized variants. Mesoporous particles were modified using two different BJH pore sizes, i.e., 2.44 and 3.76 nm, labelled as S2 and S3 particles, respectively. The immobilised enzyme showed better loading efficiency and higher enzymatic activity of mesoporous particles in both variants (S2 & S3) compared to nonporous particles (S1). The hydrolytic activity of 90% was observed for immobilised lipase compared to the free enzyme. Also, increased thermal stability with 76% reusability up to 5 cycles was reported for immobilised lipase [146]. In another study, *Candida Antarctica* lipase B (CALB) was immobilised on monodisperse core-shell magnetic nanoflowers through covalent bonding. The synthesized support possessed high saturation magnetization of (62 emu/g) with about 93 mg/g support of immobilisation yield and 22,700 U/g support hydrolytic activity. The immobilised enzyme system exhibited better pH, temperature, and storage stability than free CALB [147] (Table 1).

6. Applications of immobilised nanobiocatalysts

Immobilised nano-biocatalysts find potential applications in biotechnological, industrial and biomedical areas [12]. Compared to

existing technologies, nano-biocatalyst based technologies are simple, economical and environmentally benign [7]. Enzymes such as lipases, catalase, laccase, per-oxidases etc., are immobilised on variants of nano-supports for related bioprocess applications (Fig. 3). Additionally, various immobilised enzymes are employed to remediation and degrade several pollutants [153]. In the following sections, the applications and progress in the nano-silica based platforms for enzyme immobilisation are discussed.

6.1. Oil hydrolysis

One of the significant and essential applications of lipases is lipid hydrolysis [79]. Due to apprehensions regarding fossil fuel shortage, strategies employing bioprocessing alternatives to exploit renewable energy sources for cleaner biofuel production are burgeoning. Research towards sustainable and cleaner biofuels bioconversions and products such as biogas, biodiesel, and bioethanol is ongoing [15]. The application of immobilised lipase in biofuel/biodiesel production has been observed by many researchers [154], including the conversion of soybean oil to biodiesel fuel [155–157] and biodiesel production from waste cooking oil [158]. The immobilised lipase for biodiesel production is advantageous due to its reusability, stability and economic viability [159].

The nanomaterial supports have been used in several recent studies to immobilise enzymes for efficient enzymatic transesterification reactions to produce biofuel [160,161]. For instance, *Rhizomucor miehei* lipase was immobilised on synthesised silica nanoparticles using

Table 1
Immobilisation of various enzymes on silica nano variants.

Support material	Enzyme immobilised	Binding groups/Functionalisation	Type of Immobilisation	Cycles of recovery (reusability)	References
Wrinkled silica nanoparticles (WSNs)	β -glucosidases	Tri-ethoxysilylpropylisocyanate (TEPI)	Covalent binding	-	[148]
Hollow mesoporous silica sphere (HMS)	<i>Candida antarctica</i> lipase B	Carboxyl-functionalisation	-	60% residual activity after 8cycles	[149]
Tannic acid templated mesoporous silica nanoparticles (TA-MSNPs)	β -glucosidase	-	Adsorption	-	[150]
Silica-magnetic nanocomposite	Cellulose	APTES	-	51% enzyme activity after ten cycles	[138]
Silica-based novel biohybrid	Invertase	-	-	82% enzyme activity after eight cycles	[115]
Mesoporous silica support	β -glucosidase	Glutaraldehyde linker and silanization	Physical adsorption and covalent binding	70% of its initial activity after ten times	[98]
Spherical hollow silica nanoparticles (HSNPs)	Catalase	-	-	N.A.	[113]
Porous silica nanotubes (NTPS)	-	-	Absorption along with entrapment.	-	[116]
Mesoporous silica material (LPS)	Triacylglycerol lipase from <i>porcine pancreas</i> (PPL)	Chloropropyltriethoxysilane (CPTES) and 3-aminopropyltriethoxysilane (APTES)	-	-	[100]
Nano-silica dioxide (NSD)	<i>Porcine pancreas lipase</i>	Aldehyde groups	Covalent strategy	-	[135]
Mesoporous materials, SBA-15	<i>Candida rugosa</i> lipase (CRL)	Glutaraldehyde	Cross-linking method	80.5% of the initial activity after 6 cycles	[117]
Monodisperse silica nanoparticles (silica nanoflowers)	<i>Penicillin G acylase</i> (PGA)	Poly (dopamine) (PDA)	-	-	[151]
Mesoporous silica with different particle size	<i>Mucormiehei</i> and <i>Rhizopus oryzae</i> lipases	-	-	-	[118]
Mesoporous magnetic NPs	Lipase	3-Aminopropyltriethoxysilane (APTS) and 3-Chloropropyltriethoxysilane (CPTS)	covalent bonding, physical adsorption, and crosslinking	86.7% after ten cycles in case of covalent bonding	[145]
Single-shell nonporous (S1) and double-shell mesoporous silica nanocomposites	Lipase	-	-	76% of their initial activities after five times reuse	[146]
NH ₂ -modified magnetic silica particles	<i>Horseradish peroxidase</i> (HRP)	Glutaraldehyde	-	-	[141]
Magnetic organosilica nanoflowers	<i>Candida antarctica</i> lipase B (CALB)	-	Covalent bonding	-	[147]
Macroporous SiO ₂ -Zn nanowires	<i>Candida rugosa</i> lipase (CRL)	-	Adsorption	89.9% after 12 recycles	[152]

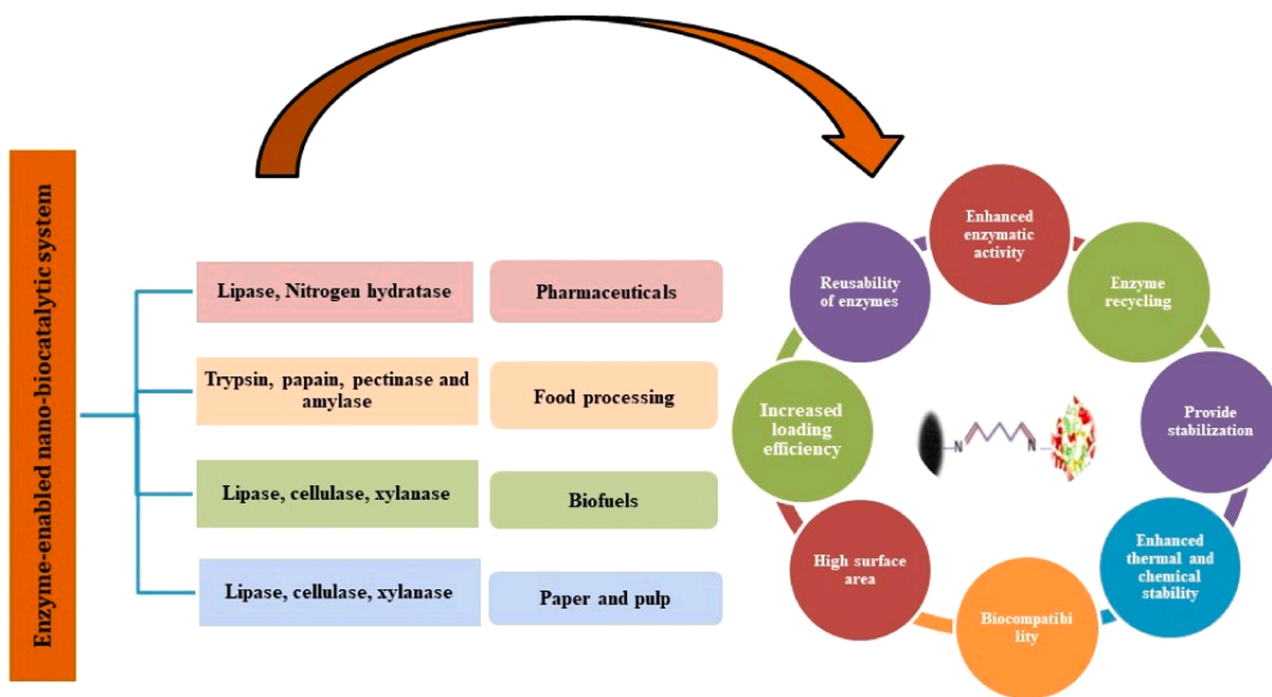


Fig. 3. Advantages and applications of nano-enabled enzyme systems.

encapsulation methodology [162]. Transesterification was carried out to produce biodiesel in the presence of methanol and triolein as substrates. An enhanced transesterification efficiency was reported in the immobilised enzyme compared to the free enzyme [162]. Tran et al. (2012) synthesised magnetic silica nanocomposite (Fe_3O_4 core with silica shell) and immobilised *Burkholderia* sp. lipase. The resulting immobilised nanocomposite system was utilised in the presence of olive oil and methanol for the production of biodiesel. The system efficiency for biodiesel production reached about 90% and demonstrated enhanced reusability and solvent tolerance ability [163]. Kalantari et al. (2013) utilised magnetic silica nanocomposite for biodiesel production. *Pseudomonas cepacia* sourced lipase was immobilised on the amino-functionalised (nonporous and mesoporous) particles by covalent strategy. The immobilised enzyme retained reusability up to 5 cycles and 55% conversion efficiency. However, when compared between the nonporous and mesoporous silica structures, enhanced stability and improved bio-catalytic efficiency were reported for the later silica structures [164]. Wang et al. (2009), reported the production of biodiesel in large reactors by immobilisation of lipases originated from *Candida rugose*, *Pseudomonas cepacia* and porcine pancreas on surface functionalised magnetic nanoparticles modified with amino groups [165]. Another study by Jun lee et al. (2012) designed nanoscale enzyme reactors by crosslinking lipase on synthesised nano-silica support. The mesostructured silica (200–300 nm) was used as a support for the transesterification of soybean oil [166]. In another study, Lipase sourced from *Rhizopus oryzae* was immobilised on mesoporous silica (MNPs) to produce biodiesel. The obtained biocatalyst system depicted 82.4% of enzyme loading and 88.4% of conversion yield, demonstrating their potential for biodiesel production [139].

6.2. Cellulose degradation

Lignocellulosic agricultural waste biomass holds strategic importance as a fuel source. Within this context, cellulase enzyme-catalyzed hydrolysis to produce glucose emerges as a potent method [167]. Second-generation bioethanol fuel, derived from glucose fermentation of lignocellulosic biomass, offers a cleaner combustion alternative to gasoline, reducing emissions such as carbon monoxide, unburned

hydrocarbons, and particulates. Moreover, bioethanol derived from biomass contributes to mitigating climate change, being CO_2 neutral [76].

Numerous studies have investigated cellulase immobilisation on various nano-supports to enhance cellulose hydrolysis. For example, Pota et al. (2022) co-immobilised β -glucosidase and cellulase onto wrinkled mesoporous silica nanoparticles with different inter-wrinkle distances. They achieved optimal performance through simultaneous immobilisation on the same vector, resulting in a biocatalyst with a 20% immobilisation yield, 82% reaction yield, and 83% retention of initial yield after 9 reuse cycles, demonstrating remarkable stability even at temperatures up to 90°C [167]. In a separate investigation, two mesoporous silica nanoparticles (MSNs) differing in particle size, pore size, and surface area were synthesized and employed as matrices for cellulase immobilisation, aiming to hydrolyze cellulose in aqueous solutions. Physical adsorption and chemical binding methods were utilized for cellulase immobilisation, with optimization of reaction conditions such as temperature, time, and enzyme quantity. The study systematically examined the loading capacity, catalytic activity, and stability of cellulase-immobilised MSN catalysts, demonstrating that cellulase chemically bound to MSNs with carboxyl groups and a large pore size achieved efficient cellulose-to-glucose conversion exceeding 80% yield with exceptional stability [168].

Yin et al. (2013) covalently immobilised cellulase on modified mesoporous silica, and the enzymatic properties of free and designed biocatalysts were investigated, compared to the free enzyme, the immobilised enzymes exhibited enhanced thermal stability, retaining 91% of their initial activity after 120 minutes at 60°C , in contrast to a 40% loss for the free enzymes. The immobilised cellulase also displayed slightly increased K_m and V_{max} values, indicating its potential for industrial cellulose degradation [169].

6.3. Bioremediation of pollutants

The upsurge in the industrial revolution has created significant concern for the environment due to the accumulation of various wastes [9] such as polycyclic aromatic hydrocarbons [170], colourants, pesticides, volatile organic components, dyes etc., [171]. Removing

pollutants from the water requires multiple strategies viz. i.) mechanical approaches, ii.) introducing microbes for bioremediation, iii.) chemicals and adsorbents [172,173]. However, direct use of immobilised enzymes helps in the remediation of such pollutants and acts as a catalyst in transferring them to less toxic or value added compounds [153]. The application of immobilised enzymes for the elimination, desolation of pollutants and the biodegradation of hazardous compounds has proven to be very efficient and selective [9]. The immobilisation of enzymes on nanoparticles increases the competence and effectiveness of the resulting system. Porous structures [174,175], such as silica nanoparticles, were most appropriate for the immobilisation purpose due to outstanding biocompatibility, hydrophilicity and ease of functionalisation capabilities, such as adsorption as well as covalent bonding [176]. For instance, Laccase from *trametes versicolor* was immobilised upon the commercial silica gel particles using a covalent strategy and activated using glutaraldehyde in the vapour phase for practical bioremediation applications. The immobilised enzyme exhibited efficient micro-pollutant degradation compared to the free enzyme. However, the biocatalyst retained its activity and reusability up to 7 cycles against pharmaceutical exclusion [177]. Chang et al. (2014) immobilised horseradish peroxidase on NH₂-modified magnetic silica particles using ultrasound-assisted co-precipitation method. The study revealed that immobilised enzymes were efficient in removing organic pollutant like dichlorophenol and more active at different ranges of temperatures and pH compared to free enzyme [141]. Numerous researchers reported various approaches for the removal of common pollutants using enzymes immobilised on nano-silica supports (Table 2). A few examples are discussed in Section 6.3

6.3.1. Pesticides treatment

The nanoparticle-based enzyme immobilisation is exploited by many researchers globally to remove pesticides, insecticides and herbicides. Dichlorophenol was transformed using fungal laccase, which immobilised on mesoporous nanostructured silicon foam. The internal pore size of silicon foam helped limit the protein denaturation and the related crowding effect within the nanostructured internal pores [178]. In another study, prolidases possessing high biodegradation capacity were utilised to treat toxic organophosphorus substances. Silica-coated magnetic nanoparticles with the combination of isocyanatopropyltriethoxysilane produced a metal-ligand complex. The resulting complex was utilised as a matrix to immobilise His6-tagged *Escherichia coli* prolidase (His6-EcPepQ). The enzyme enabled

silica-coated magnetic nanoparticles complex displayed higher activity and stability than the free enzyme. The complex was able to hydrolyze dimethyl p-nitrophenyl phosphate (methyl paraoxon) and diethyl p-nitrophenyl phosphate (ethyl paraoxon) [179], which are discrete organophosphorus compounds. In another study, amino-modified fumed nano-silica was used to support laccase immobilisation sourced from *Myceliophthora thermophila*. Suitability of the nano-biocatalyst in bioremediation by degradation of lindane was demonstrated. About 57% reduction in lindane concentration within a day was obtained. Additionally, reusability of the system up to 70% was retained after continuous seven cycles were achieved [36].

6.3.2. Dye degradation

Dyes are the most common pollutants in textile, pharmaceutical and chemical industries [180,181]. Most of them are non-biodegradable and reside for a longer duration in the environment due to their higher thermal and photo-stability characteristics. Dyes are fatal to the environment due to their carcinogenic and mutagenic properties. Various approaches are reported for dye removal using immobilised enzymes [182]. For example, nanocomposite silica-coated titanium dioxide was functionalized by amino coating, and the resulting matrix was used to immobilise ginger peroxidase. The immobilised system depicted higher potential in the elimination of acid yellow 42 dyes along with the enhanced activity and thermal stability when compared with that of free enzyme. The immobilisation enzyme produced 90% of decolourization of dye in 1.5 h, whereas the free enzyme reported about 69% of dye decolourization. On the other hand, Immobilised peroxidase reported 62% of the dye decolourization activity after six cycles of reusability [183]. In another study, two ZSM-5 zeolites with different SiO₂/Al₂O₃ ratios (Z(80) and Z(200)) were synthesized and functionalized to produce F-Z(80) and F-Z(200), respectively. These materials were utilized to immobilize laccase for the biodegradation of acid orange-7 dye, resulting in four biocatalysts: Lac@Z(80), Lac@Z(200), Lac@F-Z(80), and Lac@F-Z(200). Functionalization enhanced the stability, activity, recyclability, and storage stability of the biocatalysts, with LC-MS analysis revealing the main compounds produced from dye biodegradation [184]. Study by Das et al. (2023) systematically investigated the suitability of porous silica nanospheres (pSNs) as a nano-support for MopR, a phenol biosensor, revealing that pSNs with an average pore size of 9 nm and total pore volume of 1.12 cc g⁻¹ exhibit the highest sensitivity, detecting phenol down to 0.1 μM (10 ppb). Ni-NTA functionalized pSNs were also synthesized to refine protein-matrix

Table 2
Immobilised enzymes on silica nano-variants for bio-remediation.

Nanomaterial	Enzyme	Pollutant	% of decolourization/Enzymatic activity/ Cycles of reusability	References
Fe ₃ O ₄ microspheres and haemoglobin (Hb) with mesoporous silica, named Fe ₃ O ₄ @mSiO ₂ (Hb)	Haemoglobin (Hb)	Organic wastewater	120 U g ⁻¹ peroxidase activity	[187]
Silica gel particles	<i>Trametes versicolor</i> laccase	Micro-pollutants	7 degradation cycles. laccase activity reached 14 ± 2 U/g	[177]
'Amino modified fumed nano-silica'	Laccase	Lindane	70% activity after 7cycles	[36]
Silica nanoparticles	Horseradish peroxidase	Paracetamol	79.4% of enzymatic the activity	[188]
Silica nanoparticles	Laccase	Triclosan	65% removal rate	[189]
Epoxy-functionalized silica	Laccase	Phenolic compounds	Removal efficiency 95% after 2 h.	[190]
Mesoporous silica nanoparticles	Organophosphate hydrolases	Paraoxon(pesticide)	-	[191]
Mesoporous silica nanoparticles	Carboxylesterase	Malathion and Diethofencarb (pesticide)	The activity of the immobilised system was 50% after 22 h.	[192]
Tubular mesoporous silica containing ultrasmall superparamagnetic iron oxide nanoparticles (USPIO)	Laccase	Methoxychlor (pesticide)	Degradation rate reported upto 45.6% after 7 cycles reached to 20.8%	[193]
Mesoporous nanostructured silicon foam	Laccase	Dichlorophen(pesticide)	-	[178]
ZnO nanowires/macroporous SiO ₂ composite	Horseradish Peroxidase	Acid Blue 113, and Acid Black 10 BX(Dye)	79.4% of decolorization efficiency was retained after 12 cycles.	[194]
Fe ₃ O ₄ /SiO ₂ nanoparticles	Laccase	Procion Red MX-5B	Decolorization %percentage after 1 h was 96%,	[195]
Fe ₃ O ₄ /SiO ₂ nanoparticles	Laccase	Procion Red MX-5B, and azophloxine (phenolic dye)	Color removal of each dye by the immobilised laccase exceeded 80% in 1 h	[196]

interactions, highlighting the importance of conformational flexibility, chemical tethering, and pore volume for biosensor activity. These findings advance mesoporous nanomaterials for the development of smart biosensors in environmental xenobiotic monitoring [185]. Horseradish peroxidase (HRP) and laccase were encapsulated within a silica layer on natural silicate cores, effectively degrading pharmaceutical pollutants such as diclofenac, carbamazepine, and paracetamol. The immobilised enzymes, particularly HRP immobilised on fly ash and perlite, demonstrated high degradation rates, with complete degradation of diclofenac and paracetamol observed within three days. Immobilised laccase also showed significant degradation of paracetamol, indicating the potential of this method for pollutant removal. The immobilisation process provided stability and protection for the enzymes over three weeks, with different supports affecting enzyme activity due to their complex chemical composition [186].

7. Conclusion and future perspectives

As observed throughout the literature review, researchers have explored diverse nano-supports with inherent advantages for immobilised enzymes. With the advancement in nanotechnology, nano-particles based immobilisation offers improvement in overall enzymatic properties. The developed nano-biocatalyst finds potential in numerous applications, thus enabling their practical and industrial usage. However, certain shortcomings are associated with diverse nano-supports, such as stability, overall increased cost, toxicity, reusability, aggregation of particles, polydispersity and incapability to get functionalized with diverse groups.

In quest of exploring innovative, economic and versatile supports that can withstand the above shortcomings, advanced porous materials with tuneable pore size and high surface area can prove as a promising alternative. In this view, silica-based nano-supports can act as flexible and low-cost supports for the immobilisation of different enzymes. Silica is abundantly found in several natural forms in biota. The existing and upcoming simple and green synthesis strategies for silica extraction and its conversion into nano form have opened the gateways for the broader applicability of silica-based nano-systems in different industrial and nanotechnology-based applications. The existing advanced silica nano-supports, such as MSNs, SBA, MCF, and NTs, when coupled with different functional groups, enhance the absorption of enzymes on the supports and form stable linkages, which are advantageous for enzyme immobilisation.

Moreover, variation in nano-dimensions and other influential factors like morphology, particle size or diameter impact immobilised enzymes' properties. Strategies used to silica nanoparticles, mode of immobilisation, enzyme activity, and stability are other related significant parameters affecting the enzymatic properties are examined and reported in the literature. The present review discusses a) nanotechnologies for catalysis, b) silica-based immobilised systems and applications, c) advantages of using nano-silica based systems, d) recent and advanced technologies of mesoporous silica nanoparticle synthesis and their related applications, and e) Methods for enzyme immobilisation on various silica-based nanomaterial types is compared.

Although silica-based nano-supports have many advantages when compared to others, there are still specific challenges associated which need to be tackled for their practical and industrial applicability i.) Post-immobilisation modifications and their effect on the resulting enzymatic properties are not fully explained, requiring improvements. ii.) A profound clarity regarding parameters such as morphology, surface area, pore size and volume etc. and their influence on the enzymatic properties require further deep understanding. iv.) Limited reports on reusability and easier separation of enzymes via magnetic or advanced nanocomposites. v.) Economic precursors of silica, such as agricultural waste, are less explored for their suitability and large-scale applicability as the matrix for enabling enzymes. With the growing knowledge on enzyme immobilisation, strategies for developing newly synthesized

nanomaterials and more manageable and specific systems intended for higher efficacy of enzymes are anticipated. Novel and advanced properties of nano-support based enzyme systems should be fully exploited globally, which can find numerous applications in bio-remediation, biofuel production and detection of targeted compounds, amongst other applications.

CRedit authorship contribution statement

PJ: literature search, data curation, conceptualization, visualization, and original draft. AKM: visualization and editing draft. PK: conceptualization. PKM: editing draft. MP, CJB: conceptualization, editing draft. SM: visualization, editing draft, supervision.

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.

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