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Review

An overview on biocatalysts immobilization on textiles: Preparation, progress and application in wastewater treatment

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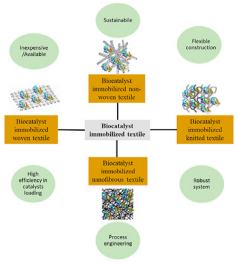
HIGHLIGHTS

- First overview on biocatalysts immobilization on textiles.
- Journey of biocatalysts immobilization on micro fibrous textiles to nanofibrous textiles.
- Biocatalysts immobilized textiles for environmental remediation application.
- Challenges, influencing factors and future considerations for biocatalysts immobilization on textiles.

GRAPHICAL ABSTRACT



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ABSTRACT

The immobilization of biocatalysts or other bioactive components often means their transformation from a soluble to an insoluble state by attaching them to a solid support material. Various types of fibrous textiles from both natural and synthetic sources have been studied as suitable support material for biocatalysts immobilization. Strength, inexpensiveness, high surface area, high porosity, pore size, availability in various forms, and simple preparation/functionalization techniques have made textiles a primary choice for various applications. This led to the concept of a new domain called-biocatalysts immobilization on textiles. By addressing the growing advancement in biocatalysts immobilization on textile, this study provides the first detailed overview on this topic based on the terms of preparation, progress, and application in wastewater treatment. The fundamental reason behind the necessity of biocatalysts immobilized textile as well as the potential preparation methods has been identified and discussed. The overall progress and performances of biocatalysts immobilized textile have been scrutinized and summarized based on the form of textile, catalytic activity, and various influencing factors. This review also highlighted the potential challenges and future considerations that can enhance the pervasive use of such immobilized biocatalysts in various sustainable and green chemistry applications.

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Contents

1. Introduction

The primary concept of catalysts involves using a material that speeds up the reaction without being consumed in the process (Rase 2000). Using suitable catalysts, the efficiency of a complex chemical process can be improved to a significant level, which led to the use of catalysts in most chemical processes these days (Gates 1992; van Santen et al., 2000). There are four basic classes of catalysts: inorganic catalysts (metals and metal oxides), organometallic catalysts (metal complexes, whose metallic core is coordinated with organic ligands), biocatalysts (enzymes), and organic catalysts (Rase 2000). Recycling of the catalysts and subsequent reuse is highly desirable from a sustainable and economical point of view (Sheldon 2007). A number of strategies have been proposed during the last decades towards achieving this goal. Among them, immobilization of catalysts or binding of catalysts to a support material (such as resins, polymers, or metals particles) without compromising their inherent properties, has gained tremendous attention from the material researchers and biotechnologists (Brena and Batista-Viera 2006; Homaei et al., 2013). However, catalyst immobilization requires complex chemical steps involving exclusive binders and resource-intensive processes, which turns the resultant catalysts into an expensive alternative to no catalysts recovery system or traditional catalytic system (Dwevedi 2016). In a typical biocatalyst immobilization process, the cost to design and prepare a support matrix is more expensive than the actual catalyst. This is the same for different enantioselective and noble organic, inorganic catalysts (Mayer-Gall et al., 2016). Considering these aspects, researchers find interest in looking for inexpensive, robust and readily available (in many versions) support materials for immobilization of catalysts. Several reports introduced textile materials as an effective support material, which provides completive benefits on above-mentioned factors, over resins, polymers or other proposed materials (carbon nanotube, gold nanostars and cellulose crystals etc.). This led to the concept of "immobilization of catalysts on textiles"- as a novel concept in the field of heterogeneous catalysis system (industrial biotechnology) as well as in technical textiles.

Textile offers flexibility in terms of size, shape, and orientation, which enables random designing of reactors suitable for a specific application. Textile further offers complete and quick separation of the immobilized catalysts while having no residues remaining in the reactor. Moreover, the open, active and porous structure of the textile surface offers low-pressure drop, which enables easy diffusion of the reaction mixture, mass transfer, and optimal substrate turnover. A substantial amount of relevant catalysts has been developed so far, which have proved to improve various chemical processes involved in the food and pharmaceutical industry due to the high stability of the catalysts on textile through strong covalent bonding (Badgujar and Bhanage 2014; Mohamed et al., 2016; Shinde et al., 2018; Al-Najada et al., 2019). In comparison to the other classes of catalysts, biocatalysts or enzymes that are capable to catalyze biochemical reactions hold a unique position due to their natural origin, moderate operating conditions (pH, temperature, and solvent), and have exceptional substrate specificity (Messing 2012). A growing interest among researchers on using enzymatic bioremediation techniques is apparent in recent literature (Sharma et al., 2018). Exceptional properties of enzymes such as *lipases*, *laccases, amylases, glucose oxidases, or peroxidases* open doors for their diverse applications in different fields including textile, food, beverage, detergent, pharmaceuticals as well as in green energy (van Beilen and Li 2002; Luna et al., 2014; Taheran

et al., 2017).

The concept of enzyme immobilization came at the beginning of 1916 and the first industrial use of immobilized enzyme was reported by (Chibata 1996). The first enzyme that has been reported to be successfully immobilized is "*invertase*", where the enzyme was immobilized on charcoal and aluminum hydroxide matrices. It has been reported that there was no loss in enzyme activity due to the immobilization (Dwevedi 2016). Since then, this exceptional advancement in biotechnology paved the way to the explosion of various methods introduced in enzyme immobilization. Enzyme immobilization has made enzymes a commercially valuable biomolecule due to various additional properties such as higher stability, more reusability, longer storage time, and a broader range of activities in presence of various physical/chemical factors. Immobilization of enzymes on textile (thus developing biocatalyst immobilized textile) further accelerated their potentiality in many instances (Chen et al., 2012). Reported that immobilized *lipase* on silk woven fabric showed a significant improvement in operational stability in the esterification reaction system. Besides, the as-prepared textile catalysts were 97% effective even after 27 batches of use which brings substantial economic benefits compared to free *lipase*s (Wang et al., 2010). intensified the synthesis of butyl oleate by using *lipase* immobilized on hydrophobic polytetrafluoroethylene nonwoven membrane, while improving the enzyme stability to catalyze the reaction up to 18 times before the productivity reduced to 91% (Mohamed et al., 2016). improved the stability of β-galactosidase enzyme by 10 °C (from 50 °C to 60 °C) after immobilizing the enzyme on plasma activated nonwoven polyester. The same textile catalysts were reported to show reusability up to 15 use cycles without a significant decrease in enzyme activity.

Narrowing from a diverse range of applications, the use of biocatalysts in wastewater treatment is gaining momentum in recent years and a number of interesting approaches have been published, involving the removal of hazardous pollutants. Eco-friendliness of the process and reuse of wastewater have been targeted and a range of complex pollutants such as heavy metals, dyes, phenols, antibiotics, pesticides, organic solvent, and pathogenic compounds have been tested (Cristóvão et al., 2011; Cristóvao et al., 2012). immobilized commercial *laccase* on coconut fibers and developed cheap and effective biocatalyst for repeated removal of textile dye (Kahoush 2019). in her doctoral thesis reported that immobilized *glucose oxidase* enzyme on carbon felt can be used as a heterogeneous catalyst to catalyze bio-Fenton and bio-electro-Fenton reaction to remove pollutants from water. In a similar approach (Gao et al., 2014), immobilized organophosphate degrading enzyme on nonwoven polyester textiles and explored their potentiality in the removal of pesticide-contaminated water. They further mentioned that immobilized enzyme used in a continuous system have shown better reaction control and effective reusability for over 60 days. Our recent studies conclusively reported the effective removal of various organic and pathogenic pollutants from water using either immobilized metal nanoparticles or immobilized enzymes on textile to produce heterogeneous catalytic systems (Morshed et al., 2019; Morshed et al., 2019; Morshed, Bouazizi et al. 2019, 2019; Nabil et al., 2019).

In catalysts immobilization, inadequate loading of catalysts, leaching of catalysts, or frictional instability have been recognized as the major drawbacks to the smooth operation and widespread application of this technology. Poor loading in turn provides poor productivity and loss of catalysts during the immobilization process. Leaching of active catalysts in the system on the other hand increases operating cost as the removal of the leached enzyme can be highly expensive due to the use of additional energy, chemical, and system interruption. Frictional instability of catalysts has been broadly addressed as the drawback of the specific system; it mainly depends on the application of the catalysts. In many systems such as wastewater treatment-frictional interaction of the catalysts is minimal. A variety of measures have been considered for tackling those drawbacks. Surface modification of support material is one of them which allows better bonding between the enzyme and the support material, reducing thus their leaching.

For more than 2000 years, chemical finishing by padding allows surface functionalization of fibers by integrating functional materials (such as functional polymers) on the textile surface through adhesive forces to yield various functionalities such as hydrophobic/hydrophilic, antibacterial, or fireproof textiles. Following the same principle of surface functionalization of textiles, robust immobilization and high loading of enzymes on fiber surfaces by integrating favorable surface functional groups (through a relatively strong bond between enzymes and textiles) has been perceived as a promising solution by many researchers (Gao et al., 2014). functionalized polyester textile with amine functional group using ethylenediamine polymer before covalent immobilization of enzymes (Mohamed et al., 2008). Reported that glutaraldehyde can be used as an efficient crosslinking agent for immobilization of *horseradish peroxidase* on nonwoven polyester fabric (Kahoush et al., 2019). modified the surface of carbon felt (nonwoven textile) with cold remote plasma (O_2 and N_2 gas) to create amine or amide groups that favor immobilization of *glucose oxidase* enzyme. Distinct functional materials have been explored for surface modification of support matrix, such as hyperbranched dendrimers (Virgen-Ortíz, dos Santos et al., 2017), metal-organic framework (MOFs) (Ma et al., 2019), and so on (Datta et al., 2020).

At the time of writing this manuscript, to the best of our knowledge, there is no report documenting the progress in "biocatalysts immobilization on textiles". However, a concise document summarizing the main points of the concept of 'biocatalysts immobilization on textiles' is necessary for researchers to navigate through the various aspects, progress, and innovations in recent publications. Therefore, we present a detailed overview of the key developments introduced in this concept based on all existing publications and patents. Considering the type of textile used as support matrix a subcategory of biocatalysts immobilized textiles can be proposed, such as (i) biocatalysts immobilized nonwoven textile, (ii) biocatalysts immobilized woven textile, (iii) biocatalysts immobilized knitted textile, and (iv) biocatalysts immobilized nanofibrous textile (see Fig. 1). Growing recent publications related to enzyme immobilization, and the use of textile as support materials are evidence of the increasing potential of this domain (see Fig. 2). The overall progress, performance, preparation methods, and application of biocatalyst immobilized textile in wastewater treatment has been discussed thoroughly to identify the gaps and possible improvement opportunities for researchers working in this domain. In the end, the challenges and prospects of this new technology have been concisely provided.

2. Fundamentals of biocatalysts immobilization on textile in brief

Since the first introduction of the concept of catalysts by chemist Elizabeth Fulhame in 1794, there has been significant development in this technology. According to (Weckhuysen 2006), 80% of chemicals that are in use in modern processes involve the use of at least one or more catalysts during their synthesis or production, which draws the picture of the vast stipulation of the catalytic process. Despite many advantages in respect to lowering the activation energy and increasing the productivity of chemical processes, the catalytic process was limited to single-use catalysts until

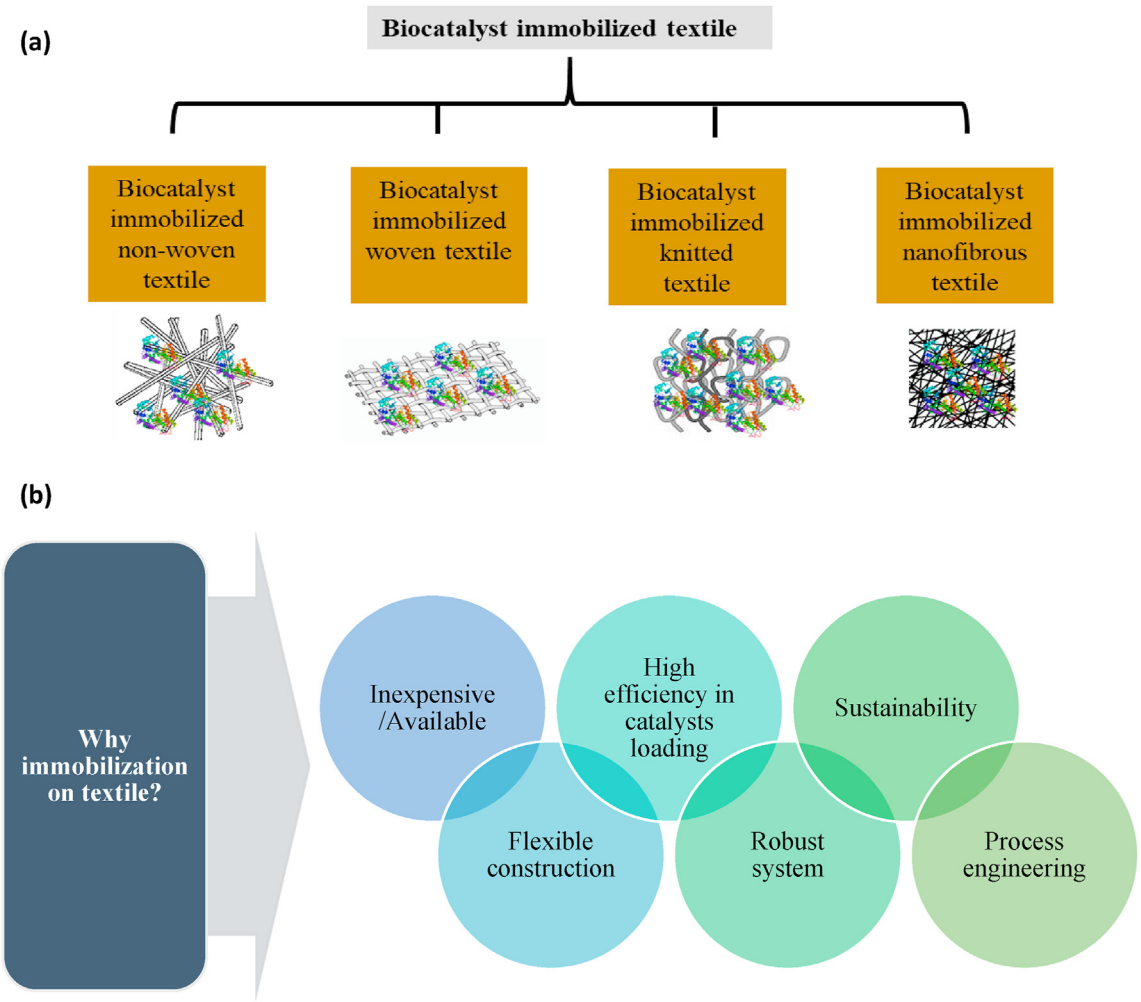

Fig. 1. (a) Various types of biocatalyst immobilized textile (biocatalyst immobilized nonwoven textile, biocatalyst immobilized woven textile, biocatalyst immobilized knitted textile, and biocatalyst immobilized nanofibrous textile); (b) benefits of using textile as a support matrix for immobilization of enzyme.

catalyst immobilization methods were introduced in the early 20th century. Since then a race to develop ideal support material for catalyst immobilization that will accelerate the efficiency of enzymes, is going on. It is often argued that an ideal support material to immobilize all catalysts is nonexistent. However, based on specific catalysts and targeted application a suitable support material can be designed (Sheldon 2007; Homaei et al., 2013). Recently, textiles have been introduced as support matrices for catalyst immobilization. Textiles have their inherent advantages like flexibility, lightweight construction, and arbitrary geometry that allows it to be used in any reactor with the potentiality of a quick separation from the reaction mixture, and the generation of residue-free product. Since first introduced by (Shemer et al., 1979), for biocatalysts immobilization on textile, almost all-basic forms of textiles have been studied for immobilization of biocatalysts. Nonetheless, apart from all-basic forms of textiles, there is a large range of possibilities of 3D and complex multi-layered textile structures for immobilization of biocatalysts or enzymes. However, in this study we have limited ourselves to the basic forms of textiles (nonwoven, woven, knitted, and nanofibrous textile). A timeline of progress in biocatalysts immobilization on various forms of textile is provided in Fig. 3.

Biocatalysts (such as enzymes) immobilized textiles are principally ideal for a robust system where strength, durability, and inexpensiveness are strategic issues. Therefore, while the catalytic property of enzyme immobilized textiles is dictated by the type of enzyme integrated, the successful integration of enzymes on the textile surface depends on the interaction between the functional group of the enzyme and the chemical nature of the polymer used for the textile fiber. The design and development of a catalytic system using biocatalysts immobilized textile is a pioneering technology, which especially focuses on the solemn problems in enzyme immobilization, specifically; cost (through inexpensive carrier material) and loading efficiency (through the tailor-made surface of textile) and robustness of the system (by reducing leaching of catalysts) and reducing the denaturing of enzymes.

A series of fibers from both natural and synthetic origin (such as cotton, wool, silk, viscose, polyamide, polyester, acrylic) have been studied to integrate different enzymes. For a robust enzyme/matrix interaction, textile fiber surfaces were tailored with amine/amide, and aldehyde as well as hydroxyl, carboxylic acid functional groups through various crosslinking/binding polymers. The possibility of covalent interaction between enzyme and support materials has been targeted for most immobilized catalysts but not for all, since covalent interaction sometimes may block access to the enzyme active sites (Albayrak and Yang 2002; Marysková et al., 2016; Al-Najada et al., 2019). Among natural and synthetic fibers, a growing interest in the use of synthetic fibers has been noticed.

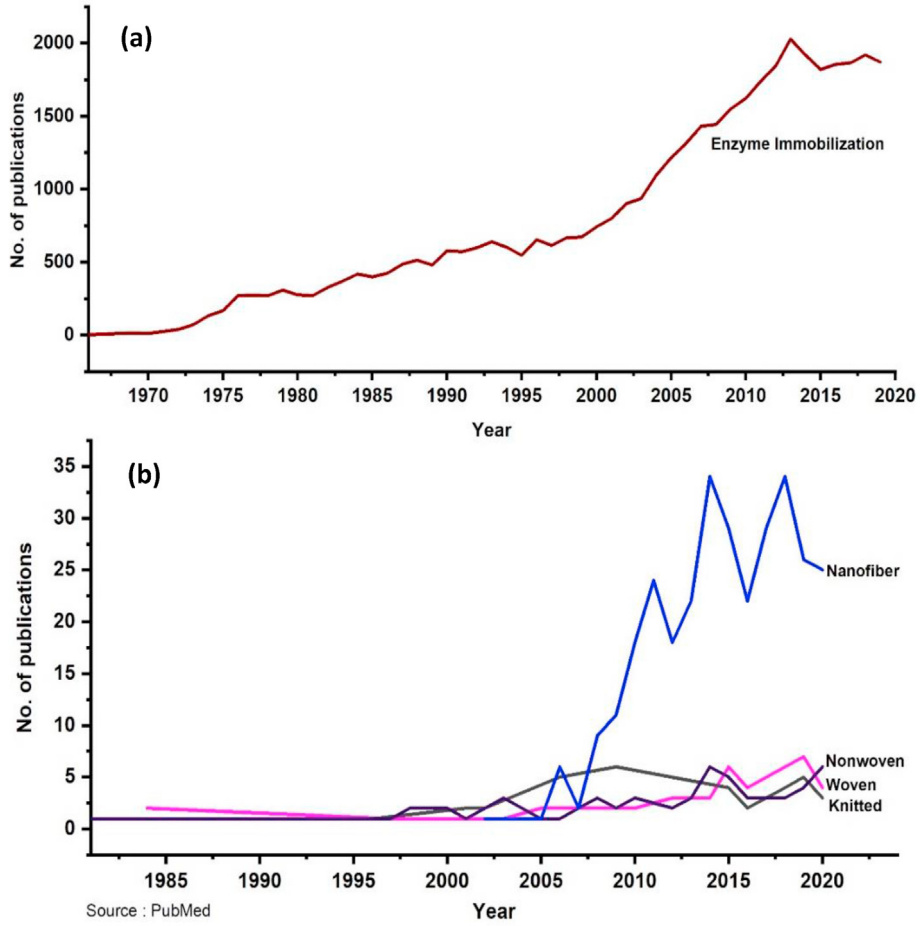

Fig. 2. Growing recent publications (until December 31st, 2020) related to (a) enzyme immobilization and (b) immobilization of the enzyme on textiles (Nanofibrous textile, nonwoven textile, woven textile, and knitted textile).

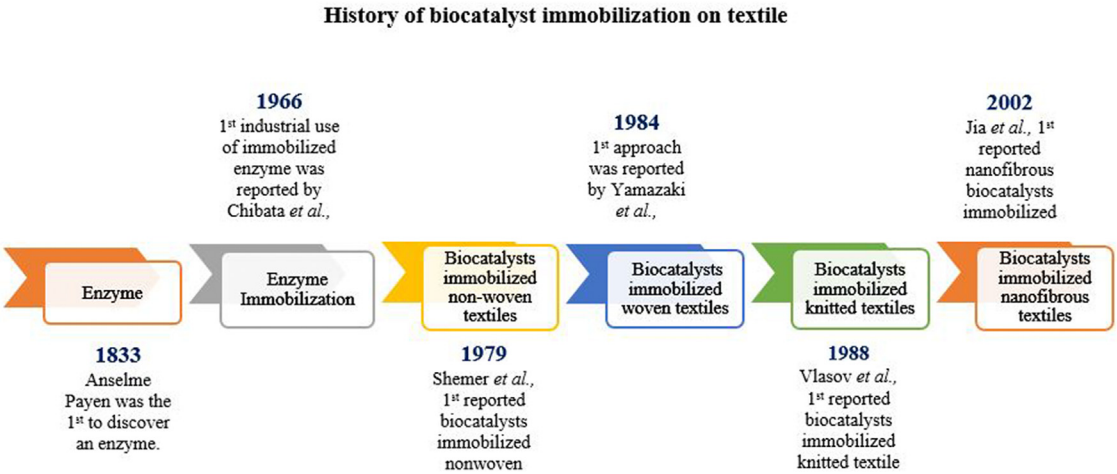

Fig. 3. Timeline of progress in biocatalysts immobilization on various form of textile, [*Anselme Payen was the 1st to discover an enzyme in 1833. The, 1st industrial use of immobilized enzyme was reported by Chibata* et al., *in 1966. Among textile as carrier matrix, Shemer* et al., *1st reported the development of biocatalysts immobilized nonwoven textile in 1979; following that Yamazaki* et al., *introduced biocatalysts immobilized woven textile in 1984; Vlasov* et al., *reported biocatalysts immobilized knitted textile s in 1988; recently (in 2002) Jia* et al., *proposed nanofibrous biocatalysts immobilized textile*].

Many researchers pointed out that, the properties of synthetic fibers are well understood. Their properties over time remain constant, and their low price make them easily accessible and affordable. Besides, their good mechanical stability and their high chemical resistance with good processability gave researchers more freedom to design a favorable surface for immobilization of specific enzymes for various applications ranging from chemical synthesis to green and sustainable chemistry.

Table 1
The influencing factors and their effects on the performance of biocatalyst (enzymes) immobilized textile in light of previous work carried by (Cao 2006).

Influencing factors	Effects on performance
Hydrophobic barrier	Enhancement of reaction rate of the hydrophobic substrate.
Microenvironment of textile	Might stabilize the enzyme.
Multipoint attachment of textile	Enhancement of enzyme wash, thermal and frictional stability.
The spacer of various types of immobilized enzymes	Prevents enzyme deactivation by avoiding essential functional groups.
Diffusion constraints	Enzyme activity decreases and stability increases.
Presence of substrates or inhibitors in textile	Higher activity retention and risk of enzyme deactivation.
Physical post-treatments	The activity and stability of enzymes can be affected.
Different binding mode	Improvement of enzyme performance.
The physical structure of the textile such as form, shape, density, porosity, pore size distribution.	Loading and fixation of the enzyme. Grasp of mass transfer limitations and inaccessibility of total fiber surface area.
Physical nature of the textile	Textiles with open structures might mitigate diffusion limitation, leading to higher activity.

The success of immobilization of biocatalysts on textile depends on several interrelated parameters. These include (1) the cost of both the enzyme and textile material. (2) The useful lifetime of the immobilized enzyme (it is desired if the used textile can be regenerated after the useful lifetime of the immobilized enzyme). (3) Binding interaction between textile and enzyme. (4) Stability and retention of enzymatic activity, which is a role of the functional groups on textile surface and the micro-environmental conditions. (5) The form, total fiber surface area, shape, density, porosity, pore size distribution, and operational stability of the selected textile will influence the reactor configuration in which the prepared Biocatalysts immobilized textile may be used. Influencing factors from the perspective of both textile and enzymes along with possible effects on the performance of biocatalysts immobilized textile has been predicted in light of (Cao 2006) and presented in Table 1.

3. Biocatalysts immobilization on textiles: performances and progress

Biocatalysts immobilized textile opens outstanding opportunities to develop a robust fiber-based catalytic system. Continuous development of this technology has expanded from microfibrous to nanofibrous textile based on the property required for the specific application. The growing success of this technology has been studied based on the common fabric form such as non-woven textile, woven textile, knitted textile, and nanofibrous textile. Here, we summarize the progress and performances of all types of biocatalysts immobilized textile based on the chronology of introduction (earliest to latest).

3.1. Biocatalysts immobilization on non-woven textiles

Nonwovens and their applications have appeared as a growing and exciting domain in textile research due to various advantages involving strength, breathability, and barrier properties. The performance of nonwoven textile on immobilization of biocatalysts (enzymes) depends on various factors, including fiber type, air permeability, porosity, thickness, fiber arrangements, and the overall fiber surface chemical property of the nonwoven. Besides, diversity in fiber types, flexible structures, and inexpensiveness of nonwoven textile attract a broad spectrum of applications.

The earliest record on immobilization of enzymes on any form of textile material was found in 1979 introduced by (Shemer et al., 1979). In the first attempt, the urease enzyme was successfully immobilized on nonwoven nylon fabric filters. They constructed multilayer immobilized-enzyme filter reactors by using a number of urease-nylon filters. Later on (Asakura et al., 1992), studied a number of nonwoven textiles from both natural and synthetic sources (silk fibroin, viscose rayon, polyester, and nylon) as effective support matrices for immobilization of redox enzymes. Results concluded that all types of nonwovens were effective as a support matrix for immobilization of enzyme (Tokuda et al., 1997). also reported the effectiveness of silk nonwoven in enzyme immobilization. They immobilized *mycelia* on silk nonwoven textile and reported that the immobilization had no adverse influence on enzymatic activity when compared to free enzymes. They further reported that the reusability of immobilized mycelia reached 10 times without significant reduction in activity.

In another study (Moeschel et al., 2003), covalently immobilized *thermolysin* enzyme on polyamide nonwoven textile showing high yields of immobilized enzyme activity with remarkably improved stability with respect to elevated temperature, pH values, and polarity (Li et al., 2011). also reported that polypropylene, polyethylene terephthalate (PET), and viscose nonwoven textiles can be inexpensive support matrices for *lipase* enzyme immobilization. They summarized that all the nonwovens were effective towards immobilizing *lipase*, allowing up to 44 cycle reuses without significant reduction in catalytic activity (Gao et al., 2014). covalently immobilized organophosphate hydrolase on PET nonwoven textile. Their study found out that, immobilization of enzyme can broaden its optimal pH stability (from pH 4.0 to pH 10.0) and enhance the enzyme stability (storage for 4 weeks without a significant loss of activity) (Mohamed et al., 2014). also reported that immobilized *inulinase* enzyme on nonwoven textile showed higher thermal (up to 60 °C), storage stability (lost about 60% by 150 days) while providing 38–44 cycles of reuses until complete inactivity of the immobilized *inulinase* enzyme (Zhang et al., 2016). Reported that immobilization of *xylanase* enzyme on polypropylene nonwoven had significantly improved in operational stability as compared to its free form.

Although a considerable study showed critical results in successful immobilization of enzymes on nonwoven textile, inadequate loading and subsequent challenges in the stability of immobilized enzyme has raised the concern for large-scale implementation. Many researchers are addressing these issues by either tailoring the fiber surface of textiles using various physical and chemical treatments or using binding/crosslinking agents. A study was done by (Mohamed et al., 2008) who reported that *horseradish peroxidase* enzyme immobilized nonwoven polyester fabric using chitosan glutamate and glutaraldehyde as cross-linking agent showed more substrates affinity than a basic nonwoven textile (Mohamed et al., 2016). Reported the activation and tailoring of polyethylene terephthalate nonwoven textile by plasma treatment provided a unique surface, that is capable of robust immobilization of *β-galactosidase* enzyme while improving the stability of immobilized enzyme significantly. In a comparable attempt (Kahoush et al., 2019), also reported the successful immobilization of *glucose oxidase* enzyme on plasma-activated fibrous carbon nonwoven (felt) textile. They showed that customized plasma treatment can integrate selective amine functional groups on carbon felt, which later influences the overall enzyme loading and subsequent catalytic performances (Iyer et al., 2020). immobilized multiple enzymes (*luciferase* and *FMN reductase*) onto polyester nonwoven textile after activating the surface through optimized plasma treatments. The plasma treatment was also reported to lead

to increase in capillary uptake of the PET nonwoven, favoring better reactional mixture flow and hence better interaction between substrates and the active site of enzymes immobilized on the nonwoven (Mohamed et al., 2008). Wunschik et al. (2020) (Wunschik et al., 2020) modified the surface of the polyester nonwoven fabric by integrating amine functional groups through chemical grafting of polyvinyl amine to achieve better adhesion and covalent immobilization of *peroxidase* enzyme. Results showed that the modification of polyester textile surface favored the loading efficiency and operation stability of immobilized enzymes. Our recent studies reported the immobilization of *glucose oxidase* enzyme on dendrimer functionalized polyester nonwoven textile (Morshed et al., 2019). We have concluded that, immobilized enzyme showed better operational stability than free enzyme. We also found that the immobilization efficiency of enzymes on nonwoven textile can be improved through a tailor-made surface with favorable functional groups.

Critical analysis of the finding from recent publications indicates that the popular nonwovens used in the immobilization of enzymes were mostly of synthetic origin. This can be due to the better control on the surface chemical property of the nonwoven textile through multiple options of modification. Consequently, the physical adsorption method of enzyme immobilization became more common for this type of textile where no binding agents are necessary. However, a considerable amount of studies also used crosslinking or covalent boding for enzyme immobilization depending on the type of fiber and application-focused. The flexible, lightweight property of nonwoven with freedom of structure makes nonwoven the desired support matrix for robust enzyme immobilization.

3.2. Biocatalysts immobilization on woven textiles

After nonwoven textiles, the woven textile is the second form of textile that has been studied for immobilization of biocatalysts (enzymes). The earliest approach to immobilize enzyme on a woven textile can be found as early as 1984 by (Yamazaki et al., 1984) where *yeast invertase* was immobilized on a cotton cloth. Following that (Kamath et al., 1988) reported the immobilization of *jack bean urease* on cotton woven fabric to prepare biocatalysts immobilized woven textiles. Resultant urease immobilized cotton cloth was used as heterogeneous catalysts for urea hydrolysis with appreciable reusability and insignificant loss in catalytic activity compared to free urease. Since then a considerable progress has been achieved.

(Li et al., 2007) immobilized *papaya proteinase* on cotton textile of twill weave. They compared the activity of immobilized and free papaya proteinase, and showed that the adaptability of immobilized papaya proteinase to environmental acidity is significantly increased, indicating the higher stability of the enzyme due to immobilization. They further identified that immobilized papaya proteinase retained more than 30% of the original activity after six continuous reuses (Opwis et al., 2004). immobilized *catalase* enzyme on one natural fiber-based (cotton) and one synthetic fiber-based (nylon) woven fabric. They reported that the integral activity of the immobilized enzyme on both cotton and nylon woven textile after 20 reuses was 10 times higher than the activity of the free, single-use *catalase*. Their findings further suggest that in both natural and synthetic fiber-based woven textile, the *catalase* crosslinked with glutaraldehyde yielded a three-dimensional structure covering the fiber-the total enzyme load was much higher than without crosslinking. When the nylon woven fabric was compared to the cotton one, it was found that cotton adsorbed a relatively higher amount of *catalase*, but the total load was doubled with covalent fixation when compared to fixation by adsorption.

(Chen et al., 2012) immobilized *lipase* enzyme on silk woven fabric (protein fiber-based fabric) functionalized with methyl groups using amino-functional polydimethylsiloxane (PDMS). They reported that immobilized *lipase*s on PDMS treated silk woven fabric were 97% effective even after 27 cycle application (Shim et al., 2017). immobilized *trypsin* enzyme on N, N′-dicyclohexylcarbodiimide, and N-hydroxysuccinimide activated polyester woven textile. They mentioned that approximately 45% of the initial enzyme activity was maintained after storage at 4 °C for 20 days, and approximately 18% of the initial activity was maintained even after reusing the immobilized enzyme 15 times.

(Song et al., 2017) reported the covalent immobilization of *trypsin* enzyme on glutaraldehyde activated woven poly (lactic acid) textile, where, the immobilized *trypsin* showed better storage stability (55% active after 20 days) and reusability (15 cycles). A recent study from (Yin et al., 2019) reported that *glucose dehydrogenase* and *bilirubin oxidase* immobilized on cotton woven textile can be used as wearable biofuel cells. It can be seen from the above discussion that, almost all types of fibers have been used as woven fabric for immobilization of various enzymes for application ranging from basic chemical synthesis to development of biocatalysts immobilized textile based biosensors and bioelectronics (Al-Najada et al., 2019). Reported that immobilized *α-amylase* on amidrazone acrylic woven textile retained 53% of its original activity after 15 cycle application and exhibited better stability against heavy metal ions, pH, temperature, and inhibitors as compared to free *α-amylase*. Overall discussion indicated that enzyme immobilization on woven textile improves the loading, stability of the enzyme and ensures robust catalyst recovery.

One of the popular microfibrous textile formation techniques is weaving, where yarns are interlaced to each other to form a woven textile. Since fibers are spun into yarn that is further woven into woven textile; there is a potential formation of microenvironment between fibers within the yarn. These microenvironments resulting in the dual-porosity of woven fabric: pores between the yarns and pores between the fibers (see Fig. 4). The former is called the inter-yarn pores and the latter the intra-yarn pores as explained by (Nierstrasz and Warmoeskerken 2003). During enzyme immobilization, it is highly desired to have an easy migration of enzyme molecules through the pores of woven textiles to achieve a uniform and long-lasting catalytic activity. However, in a typical condition, the flow resistance in the small pores of a system is higher than in the large pores. Since intra-yarn pores are smaller than inter-yarn pores, there will be a large area of textile with no flow at all. No flow translates to the inability of enzyme solutions to carry enzyme molecules to those areas of textile during immobilization. Although there have been studies related to this phenomenon concerning other porous material for enzyme immobilization or enzymatic treatment of woven textiles, yet there has been little or no detailed studies found in relation to enzyme immobilization on textiles. Evidently, an uncertainty in mass-transfer may hinder the prediction of clarity, yield, and performance of the desired biocatalysts immobilized textile.

3.3. Biocatalysts immobilization on knitted textiles

Knitted textile results from a process called knitting where inter-looping of yarns yields a knitted fabric. The properties of knitted textiles are distinct from other types of textile (nanofibrous, woven, and nonwoven) due to their higher flexibility and penetrability making them easy to use in various applications. Knitted fabrics for immobilization of biocatalysts (enzymes) were introduced after nonwoven and woven textiles by (Vlasov et al., 1988). In the study, *lysozyme* was immobilized on dialdehyde cellulose and

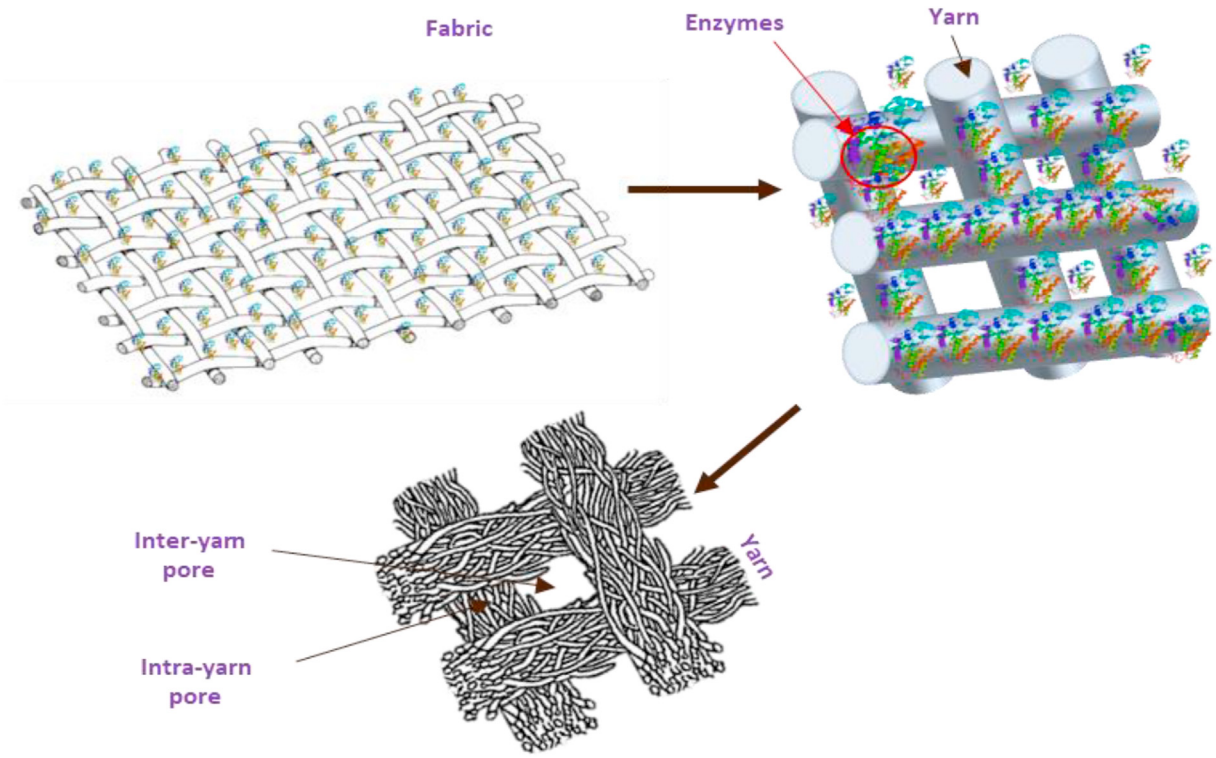

Fig. 4. Schematic illustration of enzyme immobilization on the surface, pores (inter-yarn and intra-yarn), and microenvironment of woven textile.

polycaproamide knitted textile through covalent binding to confer bacteriolytic activity. They reported that immobilized *lysozymes* were more effective in wound healing (of albino rats) than those with free lysozyme; which signifies better operational enzymatic activity of immobilized *lysozyme*.

Since the disclosure of the first potential use of knitted textile for immobilization of enzyme, considerable progress has been achieved; the area of application has expanded prominently (Nouaimi et al., 2001). directly immobilized *trypsin* enzyme on polyester knitted (fleece) textile. The study reported that immobilized *trypsin* shows higher thermal and pH stability than free *trypsin*, providing long storability for several months without losing significant activity (Albayrak and Yang 2002). studied immobilization of *β-galactosidase* on knitted (terry) cotton textile activated with p-toluenesulfonyl chloride. Results showed that the half-life of immobilized *β-galactosidase* was improved 25–28-fold (~50 days at 50 °C, and ~1 year at 40 °C) as compared to free β-galactosidase (Damle et al., 2018). immobilized *marine pectinase* on nylon 6,6 knitted textile using glutaraldehyde as a cross-linking agent. To cleave amide bonds of the nylon polymer and create more −COOH and $-NH_2$ groups on its surface, hydrolysis of nylon was carried out. They reported that, under optimized conditions, immobilization yield was found to be 78% and 69% with higher optimum temperature as compared to free pectinase providing multiple cycle reusability (Shinde et al., 2018). It was reported that polyvinyl alcohol knitted textile is an excellent support material for covalent immobilization of *alcohol dehydrogenase* enzyme. Results showed a shift in optimal reaction pH (shifting from 7 to 9), an improvement in thermal stability (by 10 °C), and adequate activity (60% active) even after 8 cycles.

From the above examples and discussions, we can estimate that knitted fabrics were effective in enzyme immobilization however, after a close look at the amount of studies carried out, knitted textile are found to be fairly less popular than nonwoven or woven textile. Mostly covalent binding or crosslinking immobilization methods were chosen for knitted textile probably due to the loose structure where the large microenvironment in fabric might play a negative role during capturing and integration of enzyme molecules. A few studies explored physical adsorption methods as well. Although an important factor for the successful enzyme immobilization is the fiber type, biocatalysts immobilized knitted textiles have been mostly used in high-end applications such as medical (wound dressing), bioelectronics (actuators), and sensors. A few other applications include chemical synthesis, environmental remediation, and so on.

3.4. Biocatalysts immobilization on nanofibrous textiles

In recent years, nanofibrous textiles have been developed using different technologies of fabrication (electrospinning, melt blown, bacteria-based natural bacterial cellulose). Different methods have been used to immobilize biocatalysts (enzymes) on nanofibers, though lots of works deal mainly with electrospun nanofibrous textiles. Lightweight nanofibrous textiles having large specific surface area, controllable pore sizes, small fiber diameters (in nanometer scale), and easy surface modification offer great potentiality in various applications ranging from tissue engineering, functional materials, and energy storage devices.

The prospect of nanofibrous textiles as a potential support matrix for enzyme immobilization was first introduced by (Jia et al., 2002) where *α-chymotrypsin* was covalently immobilized on polystyrene electrospun nanofibrous textile. They have reported a monolayer loading (1.4 wt%) of the enzyme while covering 27.4% of the external nanofiber surface with 65% of enzyme activity maintained. They also mentioned that enzyme immobilization can improve the storage stability of *α-chymotrypsin* with better resistance against organic solvents when compared to free ones. Since the first introduction in 2002, there has been a growing interest

among researchers to use nanofibrous textile as a support material for the immobilization of various enzymes (Kim and Park 2006) fabricated a mixture of biocompatible and biodegradable poly (ϵ-caprolactone) and poly (d,l-lactic-co-glycolic acid)-b-poly (ethylene glycol)-NH_2 (PLGA-b-PEG-NH_2) block copolymer-based nanofibrous textile having primary amine groups on the surface as an effective support material for immobilization of *lysozyme* enzyme.

(Ye et al., 2006) reported the immobilization of *lipase* on electrospun poly (acrylonitrile-co-maleic acid) nanofibrous with 21.2 mg/g of enzyme loading and 37.6% of relative enzyme activity maintained, which is a significant improvement compared to corresponding hollow fiber textiles (relative loading of 2.36 mg/g and relative activity of 33.9%). After that (Huang et al., 2007), further improved the relative loading (63.6 mg/g) and relative activity (49.8%) of immobilized *lipase*s by immobilizing them on chitosan/poly (vinyl alcohol) (PVA) nanofibrous textile using a coupling agent (glutaraldehyde-GA). A similar approach has been reported by (Zhu and Sun 2012), where *lipase* was immobilized on poly (vinyl alcohol-co-ethylene) (PVA-co-PE) nanofibrous membranes activated with GA. Some other reports mentioned the effectiveness of functionalizing nanofibrous textile with GA, due to the primary reactivity of GA towards amine groups, which further enables robust protein crosslinking through stable secondary amine linkages (Kim et al., 2005; Moreno-Cortez et al., 2015; Sulaiman et al., 2015). Likewise, diversity in enzyme immobilization techniques on nanofibrous textile has started to appear in many other reports as well (Li et al., 2007). covalently immobilized *lipase* enzyme on polyacrylonitrile (PAN) nanofibrous textile through amidination reaction. The resultant nanofibrous textile allowed to maintain 81% of the enzyme activity after immobilization and up to 95% of remaining activity was maintained after storage for 20 days in ambient conditions. As consistent with other reports about the reusability of immobilized enzymes, immobilized *lipase* on PAN also showed reusability of 10 repeated cycles while maintaining 70% of initial catalytic activity with the improved mechanical strength of nanofibrous textile due to the surface modifications.

(Wang et al., 2006) studied immobilization of *catalases* on poly (acrylonitrile-co-acrylic acid) nanofibrous textile with or without multi-walled carbon nanotubes (MWCNTs) and reported that nanofibrous textile with MWCNTs showed higher enzyme loading than that without nanotubes (Zhang et al., 2014). and (Wang et al., 2009) in their separate studies also reported that MWCNTs blended nanofibrous textile provides better enzyme loading and operational stability due to the efficient communications between CNTs and redox proteins (Wan et al., 2008). covalently immobilized *catalase* enzyme on alkali-treated- imide-activated poly (acrylonitrile-co-N-vinyl-2-pyrrolidone)/PAN/MWCNTs nanofibrous textile and showed evidence of better loading, high relative activity, optimal storage, pH, and temperature stability as compared to free *catalases* (Feng et al., 2012). showed a different approach of functionalization of PVA/PA6 nanofibrous textile, where they grafted metal particles [Cu(II)] on nanofibrous textile before *catalase* immobilization to achieve broader working pH, higher temperature stability, improved half-life and multiple reusabilities of immobilized *catalase* (Xu et al., 2015). used 1′-carbonyldiimidazole as a binder for immobilization of *horseradish peroxidase* on PVA/poly (acrylic acid)/SiO_2 nanofibrous textile. In this approach, 79.4% of immobilized *horseradish peroxidase* remain active while showing better storage capability (70% activity after 30 days), adequate reusability (53% of the initial activity after 10 reuses), and higher tolerance to changes in pH (3–9) and temperature (45 °C) than free *horseradish peroxidase*.

Immobilized enzymes on nanofibrous textile form a monolayer on the fiber surface (see schematically in Fig. 5a). Since the monolayer of enzymes does not allow further loading of enzymes, it limits the potential of high loading of enzymes that largely affects the overall efficiency of the catalytic reaction. Addressing the mentioned issue (Kim et al., 2005), introduced enzyme-aggregate coatings on the nanofibrous textile where at first they covalently attached a group of seed enzymes on the surface of nanofibrous textile; after that additional enzymes were cross-linked with seed enzymes and created a multilayer structure of the immobilized enzyme (see Fig. 5b). The results showed nine times higher apparent activity of the multilayered immobilized enzyme than that of a monolayer. They have further mentioned that, due to the formation of pre-organized superstructure among the covalently cross-linked enzyme aggregates on the surface of nanofibers, multilayered enzyme immobilized nanofibrous textile showed robust shaking stability for over 30 days (Cao et al., 2000). Cross-linking often refers to the loss of enzyme activity due to the blocking of active sites of immobilized enzyme, therefore, in the latest attempt, the enzyme has been reported to be encapsulated on nanofibrous textile for better substrate interaction, open sites, and an overall improvement in the stability of immobilized enzyme (see schematically in Fig. 5c). In this process, enzyme molecules were mixed with fiber polymer solution before spinning into nanofibrous textile (Dai et al., 2016). Reported the successful fabrication of *laccase* carrying electrospun nanofibrous textile where immobilized laccases retained 85.3% relative catalytic activity with better storage and operational stability.

Based on the focus of applications, the use of nanofibrous textile as a support matrix for immobilization enzyme can bring a reasonable outcome when it comes to high enzyme loading and

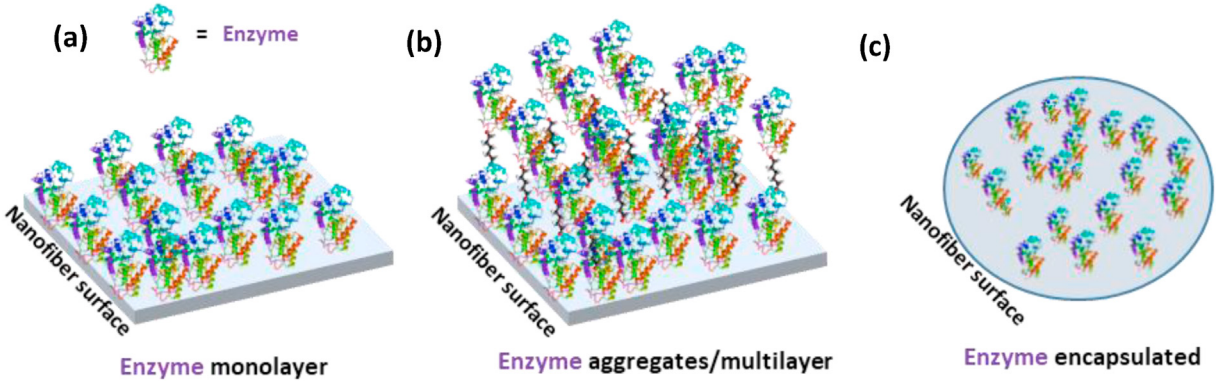

Fig. 5. Enzyme dispersion on the nanofiber surface (a) as a monolayer, (b) as a aggregates/multilayer; or (c) enzyme encapsulated inside the nanofiber.

better catalytic performance of immobilized enzymes. Besides, the consequence on pore size and permeability of reactional fluid mixture offers better mass-transfer during both enzyme immobilization (between support matrix and enzyme molecules) and catalytic activities (among enzyme molecules, substrates, and products). Nanofibrous textile provides flexibility in designing various structures of support matrix by tailoring the parameters of spinning, choice of polymers, immobilization approaches as well as surface functionalization.

4. Methods of biocatalysts immobilization on textiles

The immobilization methods play a key role in the properties and features of the biocatalysts (enzymes) immobilized textile. Among standard methods of enzyme immobilization, mostly physical adsorption, covalent binding, cross-linking, and encapsulation have been used in the design and development of biocatalysts immobilized textile. Using these methods, two different protocols of immobilization have been reported; (a) dipping/solution-based immobilization (see Fig. 6a) and (b) printing-based immobilization (see Fig. 6b). In the dipping process, enzymes and textile materials are exposed to each other in a solution medium in a standard environment, whereas in the printing process the enzymes are mixed with a solvent to prepare print ink. So far, screen, ink-jet, and valve-jet printing of enzyme immobilization of textile have been introduced as resource-efficient and eco-friendly processes. Dipping allows a comparatively higher amount of enzyme loading compared to the printing process due to open exposure of all sites of the fibrous textile at once in the solution. However, additional energy, chemicals, time, and enzyme concentrations are necessary for the dipping method compared to printing.

4.1. Physical adsorption immobilization

Physical adsorption is the simplest method of preparation of biocatalysts (enzymes) immobilized textile where adsorbed enzyme molecules bind with textile fiber surface through weak forces such as van der Waals forces, ionic, hydrophilic, and hydrophobic interactions, hydrogen bonds, and even affinity binding. The immobilization protocol consists of the activation of the textile fiber surface before being exposed to the enzyme solution in appropriate conditions. This method allows higher loading of the enzyme while the active site of the enzyme remains unaffected thus provides a good bio-catalytic activity (Homaei et al., 2013). However, this method of enzyme immobilization suffers from the desorption of enzymes due to weak physical forces that require additional attention to the carrier: enzyme interactions. A schematic illustration of enzyme immobilization by physical adsorption for the preparation of biocatalysts immobilized textile is presented in Fig. 7.

Overview on enzymes, carrier matrix, supporting chemicals,

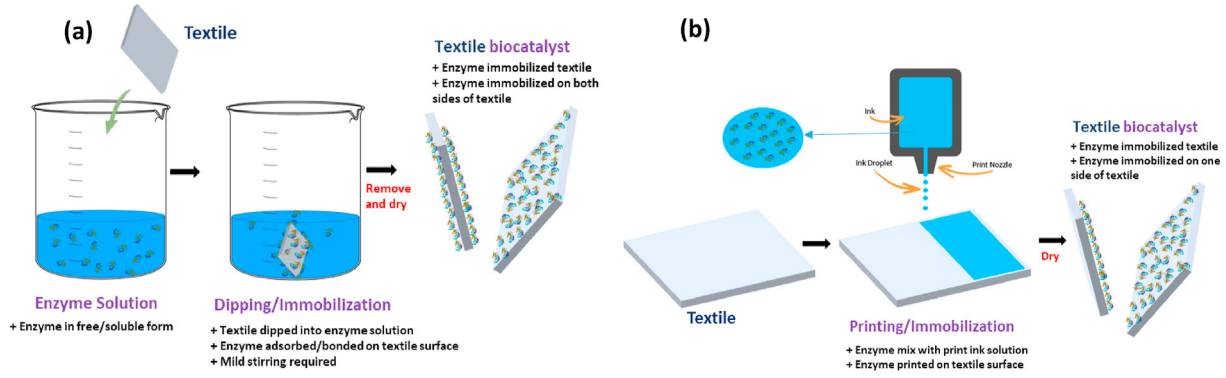

Fig. 6. (a) Dipping and (b) printing of enzyme in textile for preparation of biocatalysts immobilized textile.

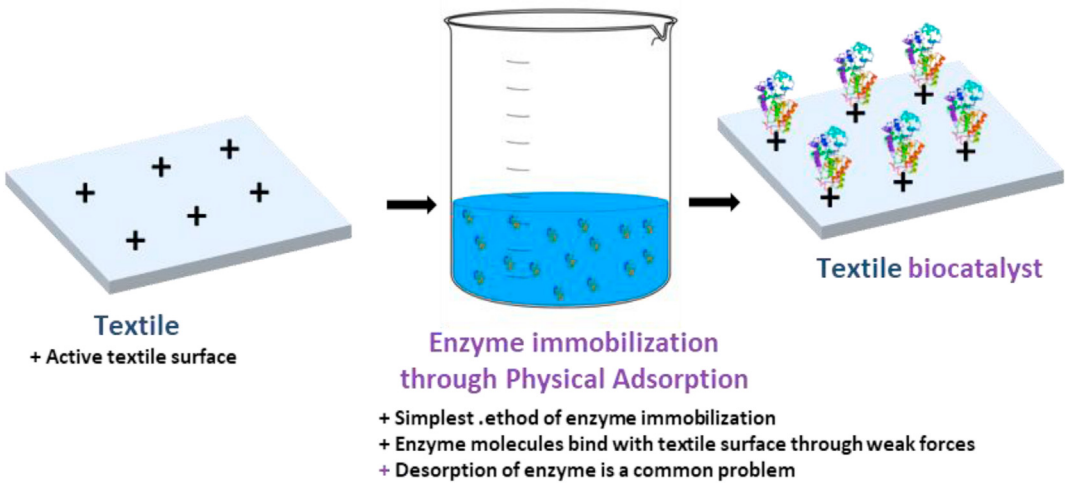

Fig. 7. Schematic illustration of the physical adsorption method for enzyme immobilization for preparation of biocatalysts immobilized textile.

Table 2
Overview on enzymes, carrier matrix, supporting chemicals, performance, and stability of immobilized enzymes on textile through physical adsorption immobilization.

Enzyme	Textile carrier matrix	Supporting chemicals/ treatments	Performance	Stability of biocatalysts immobilized textile	Ref.
β-galactosidase	Polyester nonwoven.	Plasma treatment and $CaCl_2$.	90% of sorbed enzymes maintained their activity.	The immobilized enzyme showed potential for over 15 reuses.	Mohamed et al. (2016)
Laccase	Coconut fiber-based textile.	No supporting chemical was used.	High loading of the enzyme on the textile allowed superior decolorization of all reactive dyes used in the study.	Thermal and operational stabilities were improved compared with free commercial *laccase* while maintaining 45% of activity after 13 reuses.	Cristóvão et al. (2011)
Glucose oxidase	Polyester nonwoven textile.	Hyperbranchedendrimers.	31% enzyme loading, and 81% active immobilized enzymes. Biocatalysts immobilized textile showed substantial antibacterial activity.	Immobilized enzyme retained 50% of its activity after 06 reuses with improved thermal stability.	Morshed et al. (2019)
Glucose oxidase	Carbon felt	Plasma treatment.	Resultant biocatalysts immobilized textile possess good electrical and electrochemical characteristics.	Immobilized enzymes maintained 60% of their activity after 6 reuses.	Kahoush et al. (2020)
Horseradish peroxidase	Acrylic textile	Cyanuric chloride	Biocatalysts immobilized textile in the removal of phenol from wastewater.	Immobilized enzymes retain 78% of their original activity after 10 reuses providing improved stability towards pH and temperature metal ions and some organic solvents.	Almulaiky et al. (2019)
α-amylase	Acrylic textile	Cyanuric chloride	81% of immobilized *α-amylase* enzymes remain active.	Immobilized enzyme retained 65% of the initial activity after storage at 4 °C for 8 weeks providing retained 53% activity after 15 reuses, also exhibited improved heavy metal, pH, and thermal stability.	Al-Najada et al. (2019)
Horseradish peroxidase	Wool textile	Cyanuric chloride	High yield immobilization of enzyme and good reusability has been achieved.	Immobilized enzyme retained 50% of initial activity after 07 reuses while showing broad optimum pH (7–8), improved thermal stability by 10 °C, with higher resistance to metal ions, urea, a proteolytic enzyme, detergent, and water-miscible organic solvent.	Mohamed et al. (2013)

performance, and stability of immobilized enzymes on textile through physical adsorption immobilization has been summarized in Table 2. According to the summary, the most common enzyme class that has been immobilized on textiles through physical adsorption methods are oxidoreductases (*Laccase, glucose oxidase, horseradish peroxidase,* etc) which are mostly used in biodegradation, bioremediation, or oxyfunctionalization of organic substrates.

There is a trend today among researchers, to use sustainable processes and materials such as plasma eco-technology to activate textile fiber surface or graft hyperbranched dendrimers for enzyme immobilization through physical adsorption (Kahoush 2019). stated the necessity of balanced and eco-friendly approaches to achieve efficient enzyme immobilization with minimum harmful consequences citing the health hazards and high environmental impact and provided evidence related to the potential use of eco-technologies such as cold remote plasma and a bio-based binder for immobilization of oxidoreductase enzymes on textiles through physical adsorption method. These approaches are said to be in relation to the sustainable management and design of textile-based catalytic systems.

4.2. Covalent binding immobilization

The covalent binding method is a commonly used method for the preparation of biocatalysts (enzymes) immobilized textile where enzyme molecules form a stable covalent bond with the textile fiber surface. Due to the covalent interaction between the enzyme and textile, the leaching of immobilized enzymes is minimal. The immobilization protocol requires the presence of favorable functional groups on the textile fiber surface. In many cases, it is necessary to integrate strong electrophile functional groups that will react with strong nucleophile groups present in the enzyme (as illustrated in Fig. 8). The groups that are suitable for the immobilization process can be free amino, carboxyl, hydroxyl, and sulfhydryl groups (Zhang and Xing 2011). There are three possible ways that covalent binding between enzyme and textile can take place, the first one being binding with enzyme via the side chains of lysine (ϵ-amino group) or binding with the thiol group in cysteine, or the third and most common one is to bind with carboxylic group of aspartic and glutamic acids. However, it is to be noted that, binding with any functional group on the enzyme that is essential for the activity may distort enzyme orientation and lead to unexpected denaturation. Due to these sensitive issues, precautions are involved in covalent binding, most often, the loading efficiency is comparatively low whereas the pre-treatment/modification of textile makes the process resource-intensive and costly. Covalent immobilization of enzymes has been studied for various types of textiles from both natural and synthetic origins. A number of studies reported the use of supporting chemicals which lead to covalent and stable binding of enzymes to the textile support matrices. A summary of related factors during immobilization of the enzyme on textile through covalent binding is provided in Table 3.

4.3. Crosslinking immobilization

Another popular method for the preparation of biocatalysts (enzymes) immobilized textile is cross-linking of enzymes. Enzyme immobilization by cross-linking is an irreversible method performed by the formation of intermolecular cross-linkages between the enzyme molecules by covalent bonds. In this method, nonessential functional groups in the enzyme (e.g., the amino group of *lysine* residues) can be bound to one end of the crosslinker molecule (see Fig. 9), and another end bind with functional groups at textiles surface. There are two approaches in cross-linking immobilization which are the uses of a cross-linking enzyme aggregate

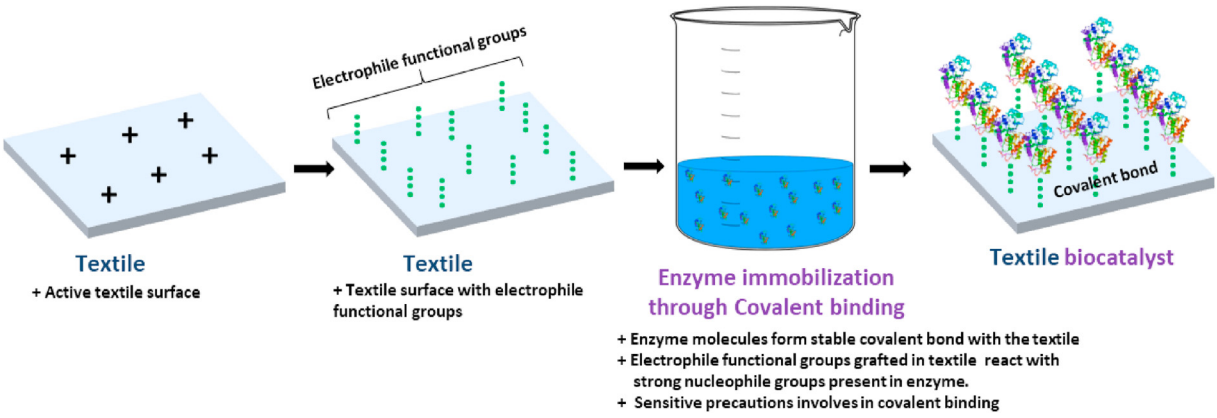

Fig. 8. Schematic illustration of the **c**ovalent binding method of enzyme immobilization for preparation of biocatalysts immobilized textile.

(CLEA), and a cross-linking enzyme crystal (CLEC). Both methods require the use of a cross-linking agent to cross-link enzyme molecules via the reactions of the free amino groups of *lysine* residues on the reactive site of neighboring enzyme molecules. It is important to find a suitable crosslinker for higher efficiency in the system since there is no ideal crosslinker for all enzymes.

The commonly used crosslinkers in the immobilization of enzymes on textiles are: glutaraldehyde, hydroxylamine hydrochloride, hexamethylenediamine, and so on. Most of them are toxic and result in severe enzyme modifications and possibly lead to enzyme conformational changes and loss of activity. Therefore, recent studies have focused on more eco-friendly alternatives which include the use of bio-based naturally occurring crosslinker (Genipin), bio-compatible polymers (chitosan, polyvinyl alcohol, polyethyleneimine), and so on, that have been reported to provide a competitive advantage over harmful crosslinkers (Mohamed et al., 2014; Kahoush 2019). Nevertheless. crosslinking method of enzyme immobilization often hinders the performance of biocatalysts immobilized textile because of poor accessibility of enzyme active site by the substrate. Based on recent studies focusing on enzymes, carrier matrix, supporting chemicals, performance, and stability of immobilized enzymes on textile through crosslinking immobilization, a summary has been structured and provided in Table 4.

4.4. Encapsulation immobilization

Encapsulation of biocatalysts (enzymes) on textile materials refers to the process, where enzymes are enclosed physically or chemically within the textile structure by either textile material itself or through a semi-permeable membrane with average membrane diameters of 100 μm or less. It also includes methods where enzymes are typically co-casted with supporting materials. Compared with other enzyme-immobilization methods introduced above, encapsulation techniques allow many enzymes to be immobilized simultaneously and the conditions used are often milder. The pore size of the textile or membrane plays a significant role in the performance of the immobilized enzyme. The encapsulated immobilized enzyme should not pass through the pore of the membrane whereas substrates and products can pass freely. Therefore, the pores of the membrane must be smaller than the size of the enzyme molecules as well as bigger than the size of substrate molecules. This essential condition for this method made it harder for many textile substrates to be considered as carrier material. Considering that, most of the attempts for enzyme immobilization by encapsulation on textiles have been carried out on nanofibrous membranes, where a tailor-made surface and pore size can be maintained. Since the enzymes are encapsulated inside the fiber, there is no need for further chemical treatment as like other methods, thus selecting the appropriate entrapment membrane might reduce the potential deactivation of enzymes during encapsulation immobilization (see Table 5). Despite many pros, limitations in diffusion between enzyme and substrate appeared as an uncompromising problem in this method compared to others.

A schematic illustration of encapsulation methods of enzyme immobilization for the preparation of biocatalysts immobilized textile is been presented in Fig. 10.

4.5. Innovative strategies for biocatalysts immobilization on textiles

There are a number of innovative strategies that have been introduced for immobilization biocatalysts (enzymes) on textiles such as digital printing (ink-jet and valve-jet), electrostatic binding (layer-by-layer deposition, electrochemical doping/polymerization), and so on (Bal et al., 2014). immobilized oxidoreductase enzymes (*Horseradish peroxidase* and *glucose oxidase*) on flexible textile fabric in predefined patterns through a new generation resource-efficient process (digital inkjet printing) (Biswas et al., 2021). studied the effectiveness of various factors in the immobilization of enzymes on synthetic polyethylene terephthalate textile surface by inkjet printing technology. In their earlier report (Biswas et al., 2019) mentioned that inkjet printing is accurate and fast enough to compete as an alternative method, but several factors such as the design of the ink, enzyme stability, and extension of the active enzyme on immobilized textiles are the vital considerations that needed to be studied deeply before considering further implementation of this approach for enzyme immobilization. Along with printing technology, electrostatic binding of enzymes on the textile surface has also been introduced as an innovative approach towards the improvement of loading and stability of immobilized enzymes on textiles (Karimpil et al., 2012). Reported the immobilization of *lipase* from *thermolysis lanuginosus* on polyethylenimine treated cotton flannel cloth through layer-by-layer self-assembly technique. They achieved a higher quantity of enzyme bound to cloth in this innovative approach. Recently (Zhang et al., 2020), reported the layer-by-layer assembly of controllable enzyme layers and loaded a high density of enzyme molecules through an electrostatic deposition.

5. Influencing factors on the performance of biocatalysts immobilization on textiles

Recent reports on biocatalysts (enzymes) immobilized textiles

Table 3
Overview on enzymes, carrier matrix, supporting chemicals, performance, and stability of immobilized enzymes on textile through covalent binding immobilization.

Enzyme	Textile carrier matrix	Supporting chemicals/ treatments	Performance	Stability of biocatalysts immobilized textile	Ref.
Laccase	Coconut fiber-based textile	3-glycidoxypropyltri-methoxysilane.	The immobilized enzyme showed higher activity and affinity towards the substrate. Which further provided high efficiency in the continuous removal of reactive dyes.	Multipoint covalent attachment of immobilized enzymes improved thermal stability (50 °C) of the biocatalyst while maintaining around 55% of initial activity after 10 reuses.	Cristóvao et al. (2012)
Organophosphate hydrolase	Polyester nonwoven	Ethylenediamine, glutaraldehyde, and methyl parathion.	Biocatalysts immobilized textile with high stability in a broad chemical spectrum can be used in the environmental remediation of pesticides.	The immobilized enzyme has broadened (from pH 4.0 to pH 10.0) its optimal pH stability. At dry state, the activity of biocatalyst remains unchanged for 4 weeks at 4 °C while a continuous 2 months use can also be possible.	Gao et al. (2014)
Horseradish peroxidase	Polyester, Polyamide, Viscose textile.	Polyvinylamine, glutaraldehyde	Crosslinking with glutaraldehyde leads to covalent and stable binding of *horseradish peroxidase* to the textile support matrixes.	The activity of one single Biocatalyst immobilized textile with immobilized enzyme stays stable over 35 successive uses. Along with that, the immobilized enzymes are storable for eight weeks under simple storage conditions.	Kiehl et al. (2017)
Horseradish peroxidase	Polymethyl methacrylate nanofibrous textile.	Polyethylenimine, glutaraldehyde.	Both free and immobilized enzymes kept more than 90% of their original activities at temperatures between 30 and 40 °C within 3 h.	At 4 °C and after 18 days, the immobilized and free *peroxidases* kept ~95% and 25% of their original activities, respectively.	Xu et al. (2013)
Horseradish peroxidase	Poly (vinyl alcohol)/ poly (acrylic acid)/ SiO_2 electrospinning nanofibrous textile.	1,1′-carbonyldiimidazole	79.4% of immobilized *horseradish peroxidase* enzymes remain active.	The immobilized enzyme showed better storage capability (70% activity after 30 days), adequate reusability (53% of the initial activity after 10 reuses), and higher tolerance to the changes in pH (3–9) and temperature (45 °C) than free enzyme.	Xu et al. (2015)
Laccase	Polyacrylonitrile nanofibrous textile.	N, N-dimethylformamide	72% relative activity of enzyme after immobilization.	Sustained more than 92% of the initial activity after 18 days of storage, while maintaining 60% of its initial activity after 10 reuses.	Xu et al. (2013)
Laccase	Electrospun chitosan/poly (vinyl alcohol) composite nanofibrous textile.	Glutaraldehyde	The removal efficiency of 2,4-dichlorophenol was about 87.6% under the optimum conditions (pH 6, 50 °C) after 6 h, which was much higher than that of free *laccase* (82.7%).	Less sensitive to changes in pH, temperature, and oscillation, thereby exhibiting higher stability and reusability.	Xu et al. (2013)
Laccase	Poly (acrylic acid)/ SiO_2 nanofibrous textile.	1-ethyl-3-(3-dimethylamino-propyl) carbodiimide, N-hydroxysuccinimide.	Performance (65% removal, 2 h) in triclosan removal than free *laccase* (29.2% removal, 2 h) under the optimum conditions (pH = 4, 30 °C).	Better storage stability and higher tolerance to the changes in pH and temperature compared with free *laccase*.	Xu et al. (2014)
Laccase	Polyacrylonitrile −biochar composite nanofibrous textile.	N, N′-dimethylformamide	Immobilized *laccase* for degradation, pharmaceutical compounds in batch experiments exhibited 72.7%, 63.3%, and 48.6% degradation efficiency after 8 h of reaction.	Immobilized *laccase* has improved storage, temperature, and pH stability compared to free *laccase*. Maintained more than 17% of its initial activity after 10 cycles, indicated improved reusability.	Taheran et al. (2017)
Lipase	Silk, cotton, polypropylene, polyethylene terephthalate, and viscose textile.	N-hexane, Tween 80, coconut oil, $MgSO_4$, polyethylene glycol, gelatin.	All textiles were effective to immobilize *lipases*. However, among them, viscose produced the most effective biocatalyst immobilized textile.	Immobilized enzymes showed operational stability of up to 35 reuses depending on the type of fiber, treatment, and co-solvents.	Li et al. (2011)
Alcohol dehydrogenase	Polyvinyl alcohol textile	Chloropropinoyl chloride, ethylenediamine, and glutaraldehyde.	Biocatalysts immobilized textile with immobilized *Alcohol dehydrogenase* provides better operational, pH, and thermal stability compared to free *alcohol dehydrogenase*.	Immobilized enzyme retained 60% of its activity after 08 reuses while shifting the optimal reaction pH from 7 to 9, and improved the thermal stability up to 60 °C.	Shinde et al. (2018)
Catalase	Cotton textile	Cyanuric chloride	A high enzyme load, high relative activity, and excellent permanence against enzyme desorption have been achieved.	Cotton textile with immobilized *catalase* maintained at least 15.5% of initial activity after 20 reuses.	Kiehl et al. (2015)
Horseradish peroxidase	Poly (vinyl alcohol)/ polyacrylamide nanofibrous textile.	Glutaraldehyde	High loading and stability of enzyme allowed the conversion of phenol in wastewater.	The resultant immobilized enzyme could be used effectively for 25 cycles with 54% retention of the activity.	Temoçin et al. (2018)

claimed that in many instances immobilized enzymes often have an activity similar or better than the free enzyme, although a look in reality at the molecular level indicates that various important factors need to be considered. Given the same environment on the application, a single unit of free enzyme will have better catalytic activity than an immobilized enzyme. This phenomenon is independent of the type and structure of support matrix used; said by (Hoarau et al., 2017). This is because, any surface (either textile or not) is not entirely neutral, therefore it interacts with the physicochemical properties of the immobilized enzyme, and hence influences the performance of the biocatalysts. For biocatalysts immobilized textile, these factors can change the overall performance of the catalysts. So, in this section, we have briefly discussed the effect of few key factors (other than reaction conditions) such as-choice of textile support matrix, nature of crosslinkers, multipoint attachments on the textile surface, enzyme orientation on the textile surface, and extent of enzyme loading on the performance of biocatalysts immobilized textile.

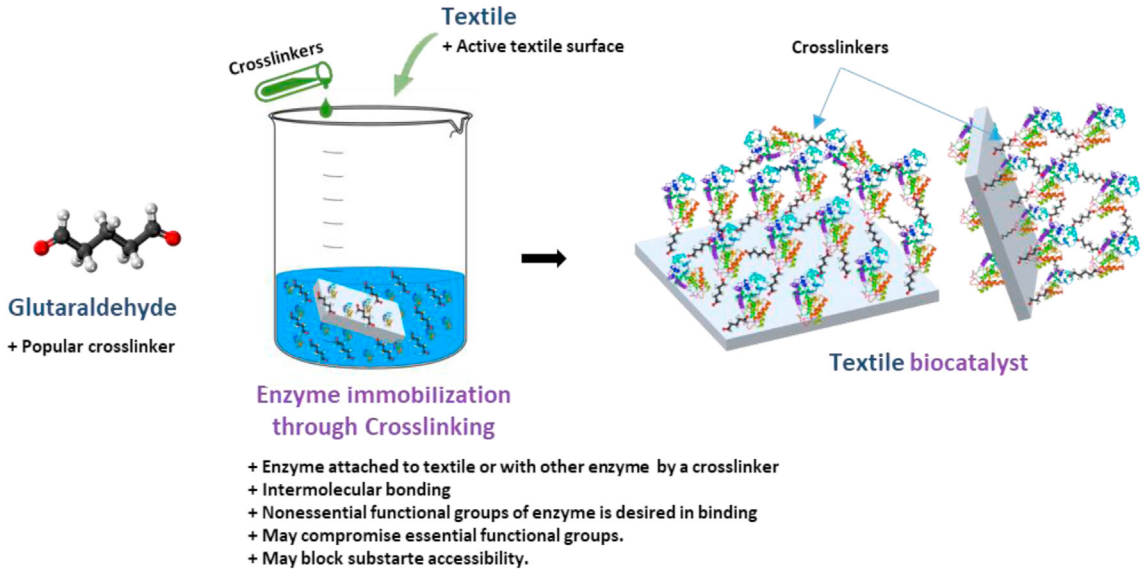

Fig. 9. Schematic illustration of the crosslinking method of enzyme immobilization for preparation of biocatalysts immobilized textile.

Table 4
Overview on enzymes, carrier matrix, supporting chemicals, performance, and stability of immobilized enzymes on textile through crosslinking immobilization.

Enzyme	Textile carrier matrix	Supporting chemicals/ treatments	Performance	Stability of biocatalysts immobilized textile	Ref.
Horseradish peroxidase	Polymethyl methacrylate nanofibrous textile.	Nanodiamond	96% of immobilized *horseradish peroxidase* remain active.	Immobilized enzyme retained 60% of its initial activity after 10 reuses.	Alshawafi et al. (2018)
Inulinase	Polyester nonwoven	Chitosan, polyethylene glycol, and glutaraldehyde.	Greater enzyme loading has been reported using different crosslinkers.	The immobilized enzyme showed higher thermal stability (up to 60 °C) while providing 38 cycles of reuses until complete inactivity of the immobilized enzymes.	Mohamed et al. (2014)
Horseradish peroxidase	Polyvinyl alcohol/bovine serum albumin nanofibrous textile.	Glutaraldehyde, Bovine serum albumin, and polyvinyl alcohol.	Loading of the enzyme on the textile support matrix reached as high as 27.3% (w/w).	Immobilized enzyme retained 73% of its activity after 11 reuses.	Fazel et al. (2016)
Trypsin	Polyester nonwoven	Chitosan, Glutaraldehyde	High enzyme loading provides potentiality for multifunctional application of biocatalyst immobilized textile.	Resultant immobilized *trypsin* showed 50% of its initial activity after 15 reuses and 80% of that after 20 days of storage at 4 °C.	Kim and Lee (2019)
Laccase	Polyacrylonitrile-biochar composite nanofibrous textile.	Hydroxylamine hydrochloride	Degradation of chlortetracycline in continuous mode exhibited 58.3%, 40.7% and 22.6% chlortetracycline removal efficiency at flux rates of 1, 2 and 3 mL/h · cm^2.	Immobilized *laccase* showed improved storage, temperature, and pH stability compared to free laccase.	Taheran et al. (2017)
Laccase	Polyamide 6/chitosan nanofibrous textile.	Bovine serum albumin and hexamethylenediamine	A6/CHIT-*laccase* biocatalysts to eliminate a mixture containing 50 μM of two endocrine-disrupting chemicals: bisphenol A and 17α-ethinylestradiol.	Efficient in the removal of a mixture of endocrine-disrupting chemicals in three treatment cycles.	Maryšková et al. (2016)
Lipase	Polyvinyl alcohol/alginate, polyethylene oxide/alginate nanofibrous textile.	Glutaraldehyde	Resultant Biocatalysts immobilized textile has been proposed to be effective in biodiesel production, transesterification, aminolysis, and alcoholysis.	Immobilized enzymes maintained up to 60% of their activities after 14 reuses with improved pH and thermal stability.	Doğaç et al. (2017)
Trypsin	Polyester fabric	N, N′-dicyclohexylcarbodiimide, N-hydroxysuccinimide, and Glutaraldehyde	The established optimum condition for preparation of Biocatalysts immobilized textile with high loading and stability of the enzyme.	Immobilized enzyme maintained 45% of the initial activity after storage at 4 °C for 20 days, and approximately 18% of the initial activity even after 15 reuse.	Shim et al. (2017)
Glucose oxidase	Carbon felt	Genipin crosslinker	Resultant biocatalysts immobilized textile showed better stability as well as good electrical and electrochemical characteristics.	Immobilized enzymes maintained 40% of their activity after 6 reuses.	Kahoush (2019)

Table 5
Overview on enzyme, carrier matrix, supporting chemicals, performance, and stability of immobilized enzymes on textile through encapsulation immobilization.

Enzyme	Textile carrier matrix	Supporting chemicals/ treatments	Performance	Stability of biocatalysts immobilized textile	Ref.
Laccase	Laccase-carrying electrospun fibrous textile.	No supporting chemical was used	85.3% relative active *laccase* immobilization has been achieved (vs free *laccase* solution).	Better storage and operational stability of immobilized *laccase* compared to free *laccase*.	Dai et al. (2016)
Horseradish peroxidase	Poly (d,l-lactide-co-glycolide)/ PEO−PPO−PEO (F108) electrospun fibrous textile.	No supporting chemical was used	Resultant Biocatalysts immobilized textile showed excellent removal efficiency of phenolic contaminants.	The immobilized enzyme showed better stability towards temperature, humic acids while retaining retained over 50% of initial activity after 02 months (30% after 03 months).	Niu Xu et al. (2013a,b,c)
Laccase	*Laccase*-carrying electrospun fibrous textile.	No supporting chemical was used	88.9% relative active *laccase* immobilization has been achieved (vs free laccase).	Better storage and operational stability of immobilized *laccase* compared to free *laccase*.	Dai et al. (2016)

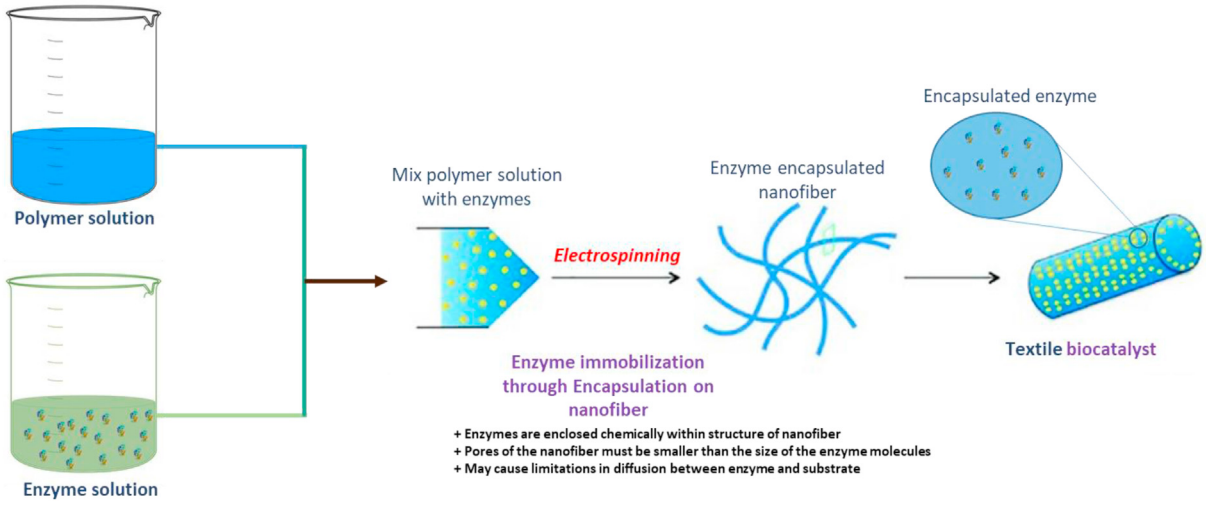

Fig. 10. Encapsulation method of enzyme immobilization for preparation of biocatalysts immobilized textile.

5.1. Choice of the textile support matrix

The choice of textile structure and type of fibers is paramount in determining the success of immobilization and appropriate activity of the biocatalysts (enzymes) immobilized on the textile. The selection of the suitable fiber type can significantly affect the immobilization process. The type of fiber dictates the end-terminal groups present as well as the surface physico-chemical properties of the textile fiber. This is a key for enzyme stability as demonstrated in a study by (Opwis et al., 2014), where they have studied and compared polyester (PET), polyamide (PA) or cotton as alternative carrier materials for the immobilization of enzymes.

5.2. Nature of crosslinkers

Direct anchoring of biocatalysts (enzymes) to the fiber surface of textile has been the most frequently used strategy to immobilize enzymes. However, from the discussions in previous sections, many reports indicate that, despite the type of fibers used, the raw surface of textile does not provide the best surface condition for enzyme immobilization, especially in the case of a charged, hydrophilic or hydrophobic surface. Some reports suggested that the interaction between enzyme and raw surface could result in the enzyme unfolding once immobilized (Zhao et al., 2015). (Chen et al., 2015) once reported that direct anchoring of *lipase* on a hydrophilic surface-induced significant deformation of the protein structure. On the other hand, hydrophobic surfaces can also interact with the hydrophobic side-chains of enzymes and may cause denaturing of enzymes. To solve the problem related to the hydrophilic and hydrophobic surfaces for any particular enzyme, a crosslinker that works as a bridge between the textile surface and the enzyme surface will limit the interaction and improve the stability of the enzyme. A crosslinker can control the overall loading, stability, and performance of a biocatalyst. A number of crosslinkers has been reported for crosslinking of enzymes or for covalent immobilization of enzymes on textile support matrix. Common phenomena of choosing amine-rich crosslinkers has been noticed in many reports (Chen et al., 2012). immobilized *lipase* enzyme on textile using amino-functional polydimethylsiloxane (PDMS) crosslinking (Damle et al., 2018). immobilized marine *pectinase* on polyamide textile using glutaraldehyde as a cross-linking agent (Wunschik et al., 2020). immobilized peroxidase enzyme on polyester textile using polyvinyl amine as a crosslinker through covalent bonding. New eco-friendly, bio-based naturally occurring crosslinker, biocompatible polymers such as Genipin chitosan, polyvinyl alcohol, polyethyleneimine have been reported to crosslink enzymes on textiles (Mohamed et al., 2014; Kahoush 2019). Although crosslinkers help in enzyme loading and stability, they are not entirely neutral when it comes to changing the physicochemical properties of enzymes that may further modify the affinity of the enzyme

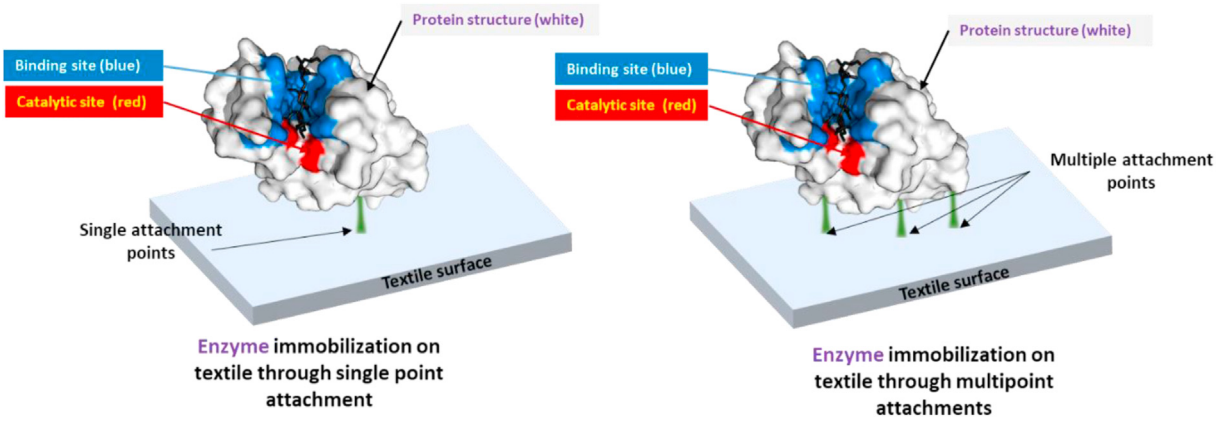

Fig. 11. Schematic illustration of single and multipoint attachment of enzyme on support matrix during immobilization.

towards substrates. Therefore, a suitable selection of crosslinkers based on specific enzyme and support matrix is a precondition for a robust bio-catalytic system with high enzyme activity and stability.

5.3. Multipoint attachments on the textile surface

Biocatalysts (enzyme) immobilized on the textile surface can be bound through either a single and multipoint attachment as illustrated in Fig. 11. This type of phenomenon is more visible in the covalent binding method for enzyme immobilization. Multipoint attachments of the enzyme may demonstrate stabilizing effects on a wide range of enzymes. Multipoint attachments on the textile surface are relatively difficult to achieve because the formation of multiple linkages between enzyme and surface can potentially result in distortion of enzyme structure if the linkages are not well matched. Thus the approach requires careful optimization of the textile surface while maintaining optimum reaction conditions (Mateo et al., 2006).

A report by (Barbosa et al., 2013) postulates that multipoint attachments occur, with fixation at parts of the enzyme, however, they usually involve only one type of reactive functional group, typically the primary amino group of lysine residues for which the reactivity can be tuned by careful pH monitoring. A report by (Mateo et al., 2006) demonstrated that, with a successful multipoint attachment of enzyme to a carrier material, the stability of enzyme can be amplified by 1000–10,000 times compared to that of free enzyme. So far, no report has been found that conclusively studied for multipoint attachments on the textile surface. However, based on a look at molecular level it can been found that, a typical multipoint attachment of enzyme at the textile fiber surface might occur when the reaction of the first residue anchors the enzyme to the surface of textile, and the other reactive unused reactive functional group in enzyme further interacts with neighboring residues of the support materials. A limitation of this strategy is the need to maintain protein dynamics and large-scale protein motions that are essential in many enzymes for substrate binding, product release, and chemical catalysis.

5.4. Biocatalyst (enzyme) orientation on the textile surface

The orientation and three-dimensional structure of immobilized enzymes are crucial to ensure high enzyme stability and activity. Since the orientation of the enzymes cannot be actively controlled by the immobilization methods, this might result in unexpected but unavoidable burying, which further causes the inaccessibility of the active site of the immobilized enzymes. During the immobilization process, enzyme molecules undergo substantial changes in terms of the surface microenvironment, conformation, and protein refolding. Many challenging questions in the biosensor field and the development of sophisticated biocatalyst for wide biotechnological applications can be solved by controlling the orientation of individual enzymes, as well as their homogeneity during coating. The face of the active site of the enzyme to be accessible by the substrate solution is the primary condition for a bio-catalytic activity to occur. During immobilization of enzymes, most of the immobilized enzymes that lose their activity by denaturing are due to the wrong orientation of the enzymes at the surface of the support matrix (as illustrated in Fig. 12). Therefore, the orientation of enzyme on textile fiber surface after being immobilized is an important factor that influences the performance of the biocatalysts immobilized textile. Proper orientation of enzyme on the textile surface will provide a number of benefits, namely; the activity of all immobilized enzyme, improved enzyme-substrate interaction, reduce the effect of surrounding stimuli in the activity of the enzyme, limit use of essential functional groups during covalent or multipoint attachment and finally, the active site of enzyme will be less exposed to deformation or rigidification (Hoarau et al., 2017). once reported that, among common methods of enzyme immobilization, physical adsorption may lead to the selective orientation of enzyme on support matrix, however, covalent attachment is more efficient on the precise orientation of enzymes (Godoy et al., 2011). found out that, proper orientation of enzyme can significantly improve the stability of the immobilized enzyme. They have reported that immobilized *lipase* with active site pointing towards bulk solution showed better stability towards organic solvents than enzyme immobilized in a disoriented way.

5.5. The extent of biocatalysts loading

The amount of biocatalysts (enzymes) loaded on biocatalysts immobilized textile will affect the activity and performance of the biocatalysts. Most of the research conducted on immobilizing enzymes on textile surfaces focused on the loading efficiency of the enzymes on textile (Mohamed et al., 2008; Song et al., 2017; Morshed et al., 2019). Various modification of textile surface has been carried out for higher loading as discussed earlier. However, it is to be noted that, excessive loading of the enzyme on the surface of the textile may trigger negative effects which may be deleterious for enzymes, causing deformation/compression of enzyme structure and limiting solvation and fast accessibility of active site of the enzyme by the substrates (Hoarau et al., 2017). A limit of enzyme loading on a support matrix can be identified by the imbalance

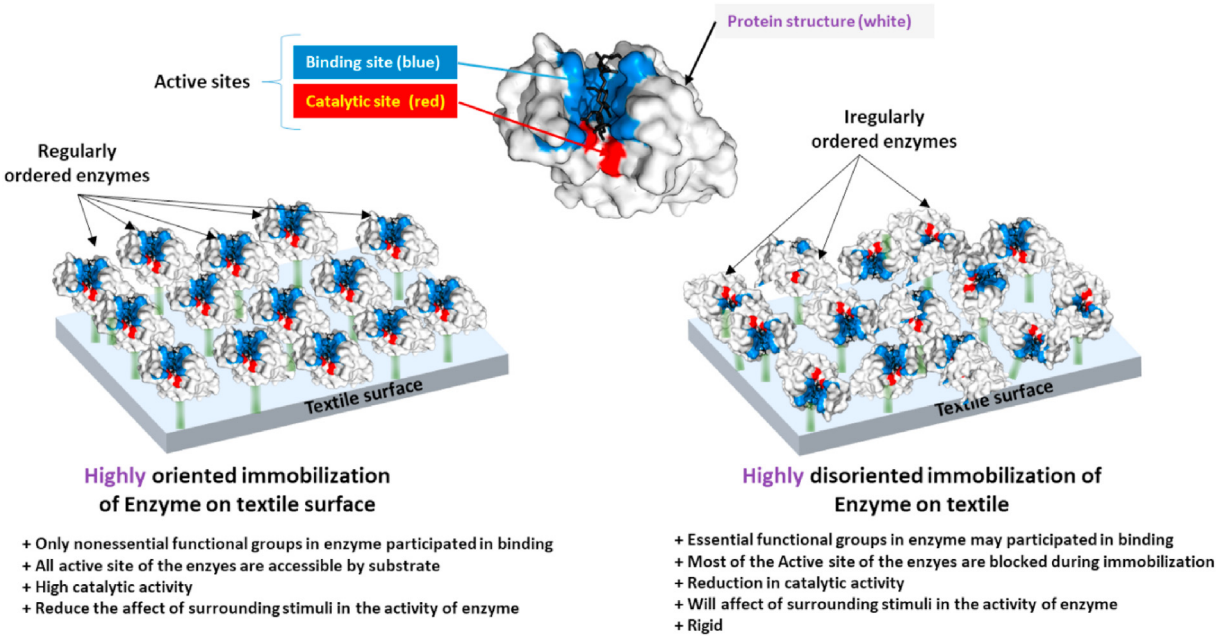

Fig. 12. Schematic illustration of how the orientation of immobilized enzyme affects the activity.

between diffusion rate and immobilization rate. A typical case for overloading of the enzyme can be identified in crosslinking methods of enzyme immobilization: the formation of cross-linked enzyme aggregates indicated that the enzyme formed patches at the surface as explained by (Badgujar and Bhanage 2014). This problem might affect the preparation of biocatalysts immobilized textile adversely through an uneven distribution of the enzyme since a high concentration of enzyme will be present at the external surface of the textile, whereas a low concentration of enzymes will be inside the pores, which will decrease the catalytic activity, increase the cost of the operation due to the waste of enzymes. To avoid this situation, and optimization of the concentration of the stock solution of enzyme needs to be determined before immobilizing on the textile surface (Fernandez-Lopez et al., 2017). suggested that although high loading of the enzyme is desired in many cases, low enzyme loadings should also be considered (if a uniform distribution cannot be accomplished) to avoid losses in overall efficiency.

5.6. Mass transfer and diffusion limitations

Mass transfer and diffusion effect of substrate and the product is very important in the successful catalytic actions of the immobilized biocatalysts (enzymes). Although this is a critical factor before designing an enzymatic system, a limited extent of studies related to immobilization of enzymes on textiles addressed this issue, hence this part of the overview is limited to the hypothetical discussion.

Immobilization of enzymes on textiles typically raises resistance to mass transfer. For determining the kinetics of biocatalysts immobilized textile, internal mass transfer and diffusion limitation of the enzyme, substrates, and products need to be taken into consideration before designing a system using biocatalyst-immobilized textile. In a complete process involving immobilization of biocatalyst immobilized textiles and their catalytic application, diffusion limitation affects the performance of both (i) immobilization and (ii) catalytic application. In the first case, optimal loading of the enzyme on the textile support matrix during immobilization could not be achieved as poor diffusion blocks enzyme molecules to reach many areas of textile (correlated differences inflow on the intra-yarn and inter-yarn pores —discussed in ***section 3.2*** above). In the second case, in a porous support matrix such as textile, diffusion, and reaction occur simultaneously since biocatalysts are immobilized on fiber surfaces of the internal pores, therefore substrates diffuse through those pores and react with enzymes. Diffusional limitations in biocatalyst-immobilized textile involve a number of factors such as the structure of textile, type of fiber used, surface treatments, the size of enzyme molecules, and solvent used (Nierstrasz and Warmoeskerken 2003). Increase capillary uptake by plasma activation of fibers in the outer and inner textile layers can increase the inflow of enzyme solution through the inner textile and allow enzyme immobilization on fiber surfaces in the inner parts of a microfibrous nonwoven (Kahoush 2019). As summarized by (Feng et al., 2012), among all four forms of textile structures, nanofibrous textile shows a better binding capacity of immobilized enzymes and, increases the mass transfer kinetics. Earlier (Huang et al., 2007), reported that nanofibrous textile with small fiber diameter (80–150 nm) could provide a large specific surface area and create a more favorable interface for the mass transfer of substrate or product to or from the active site of the enzyme. Few other studies mentioned the high mass transfer of nonwoven textile as well, whereas the highest diffusion resistance occurs in the woven structured textiles (Chen et al., 2012; Song et al., 2017; Kahoush et al., 2019; Morshed et al., 2019). Although this is not an ideal conclusion, but this phenomenon predominantly indicates that, rigidity and compactness impart poor diffusion than that of open loose-structured fabrics. There have been many reports based on speculative assumptions, but a detailed study on mass transfer and diffusion limitation related to immobilization of biocatalysts on textile support matrix is yet to be done. In addition to fiber diameter and density, the core issue regarding the mass transfer and diffusion limitation can be narrowed down into two key issues (a) pore size of the textile matrix and (b) particle size of the biocatalyst. According to Riet and Tramper (1991) (Van't Riet and Tramper 1991), for any support material for enzyme immobilization, the diffusion limitation can be minimized by decreasing

the particle size of the biocatalysts or increasing the pore size of the support matrix. Although it is not often the most desired option when designing a reactor, this idea remains the most common and widely used solution.

6. Stability of biocatalysts immobilized textiles (pH, temperature, storage)

One of the reasons for biocatalysts (enzymes) immobilization is to improve the stability of enzymes during long-time storage or in various situations of work such as different temperatures or pH values. To evaluate these parameters, researchers usually compare the immobilized and free enzymes (Nouaimi et al., 2001; Albayrak and Yang 2002; Mohamed et al., 2008; Shim et al., 2017; Damle et al., 2018; Shinde et al., 2018; Al-Najada et al., 2019). By analyzing the literature, where authors claimed to improve the pH, temperature, and storage stability of immobilized enzyme on textile, it can be seen that immobilized enzymes were found to be stable and active at lower pH values, performing well at 60 °C and improving their thermal stability for temperature increase by 10–15 °C, compared to free enzymes. (Mohamed et al., 2008), reported that immobilized *Horseradish peroxidase* on nonwoven polyester fabric showed improved stability with higher thermal stability improved by 10 °C compared to the soluble enzyme. A similar report finding has also been reported by (Shinde et al., 2018) were, they observed a shift in optimal reaction pH from 7 to 9 and a 10 °C temperature increase for covalently bound *alcohol dehydrogenase* enzyme on PVA knitted textile (Albayrak and Yang 2002). also reported that, after immobilization of *β-galactosidase* on cotton textile, the half-life and temperature stability was improved 25–28-fold as compared to free β-galactosidase (Shim et al., 2017). showed that immobilized trypsin enzyme on polyester woven textile can be stored for 20 days at 4 °C while maintaining more than half of the initial activity (Song et al., 2017). showed that immobilized *trypsin* enzyme on poly (lactic acid) textile maintained 55% of its initial activity after 20 days of storage. The overall discussion indicated that, immobilization of enzyme certainly improves the stability of an enzyme, thus it is safe to say that, pH, thermal and storage stability of biocatalysts immobilized textile is usually higher than that of free enzymes which will give competitive benefits in a wide range of applications.

7. Reusability of biocatalysts immobilized textiles

The main concept of immobilization was inspired by the potentiality of the recycling and reuse of biocatalysts (enzymes). In order to compensate for the costs of enzyme immobilization, it is highly desired that the immobilized enzyme have the potential to be reused for a number of cycles. A close look at the literature on enzyme immobilized textile shows that, satisfying the basic concept of immobilization, all enzyme immobilized textile showed easy recyclability and reusability from 03 times to up to 44 times (Li et al., 2011). Immobilized *lipase* enzymes on silk woven fabric were 97% effective even after 27 cycle application (Chen et al., 2012). Immobilized trypsin maintained activity even after reusing for 15 times (Shim et al., 2017; Song et al., 2017). *Lipase* immobilized on nanofibrous textile has reported showing 05-to 35-cycle application depending on the type of support matrix, and the corresponding functionalization used (Huang et al., 2007; Li et al., 2011; Zhu and Sun 2012; Doğaç et al., 2017). Al-Najada et al. (2019) (Al-Najada et al., 2019) reported that immobilized *α-amylase* retained 53% of its original activity after 15 cycle applications. Even though, it is difficult to compare various research works together in the case of reusability when they use different methods and conditions to check the reusability. Yet, it was evident that high reusability of the enzyme immobilized textile can be achieved through tailor-made surface preparation of textiles and immobilization strategies.

8. Application of biocatalysts immobilized textiles in wastewater treatment

Immobilized biocatalysts (enzymes) in general present various advantages over free enzymes, especially in terms of reusability, easy separation, and higher stabilities (pH, thermal, storage) (Defaei et al., 2018; Shakerian et al., 2020) as discussed in previous sections. As summarized in Table 6, biocatalyst immobilized textiles (immobilized enzymes on textile support matrix) have been found to be useful in various applications ranging from-food preparation and preservation, pharmaceuticals and medical devices, fine chemical synthesis, biodegradation, bioremediation, wastewater treatment application, and so on. Among them in this section, we have overviewed the growing use of biocatalyst immobilized textiles in wastewater treatment applications and these are summarized in Table 7.

Table 6
A brief overview of biocatalysts immobilized textile and their primary focuses of application.

Type of biocatalysts immobilized textile	Most targeted Enzyme classes	Most used immobilization methods	Primary focuses of application
Biocatalysts immobilized nanofibrous textile	+ Oxidoreductase	+ Encapsulation> + Crosslinking > + Physical adsorption	+ Biodegradation, bioremediation, and environmental application. + Oxyfunctionalization of organic substrates. + Diagnostic and biosensors.
Biocatalysts immobilized woven textile	+ Hydrolases + Oxidoreductase	+ Covalent binding > + Crosslinking	+ Pharmaceuticals and Fine Chemical synthesis. + Food preparation and preservation. + Biodegradation, bioremediation, and environmental application.
Biocatalysts immobilized non-woven textile	+ Oxidoreductase + Hydrolases	+ Physical adsorption> + Crosslinking > + Covalent binding	+ Biodegradation, bioremediation, and environmental application. + Oxyfunctionalization of organic substrates. + Pharmaceuticals and fine chemical synthesis. + Food preparation and preservation.
Biocatalysts immobilized knitted textile	+ Oxidoreductase + Hydrolases	+ Covalent binding > + Crosslinking > + Physical adsorption	+ Food preparation and preservation + Pharmaceuticals and medical devices. + Fine Chemical synthesis + Biodegradation, bioremediation, and environmental application.

> = more frequent than.

Table 7
A summary of removal of pollutants from wastewater using biocatalyst immobilized textiles.

Pollutants name	Pollutants category	Enzyme used	Pollutants removal, %	Reusability cycles	Ref.
Chlortetracycline, Carbamazepine, and Diclofenac	Pharmaceuticals	*Laccase*	48.6–72.7%	10	Taheran et al. (2017)
Reactive Black 5, Reactive Blue 114, Reactive Yellow 15, Reactive Yellow 176, Reactive Red 239, and Reactive Red 180.	Dyes	*Laccase*	~90-96% (individual) -45-63% (mixed)	2	Cristóvão et al. (2011)
Remazol blue RR	Dyes	*Glucose oxidase*	93.0%	6	Kahoush (2019)
Methyl parathion, Coumaphos	Pesticides	*Organophosphate hydrolase*	~100%	NR	Gao et al. (2014)
Staphylococcus epidermidis, Escherichia coli	Pathogenic contaminants	*Glucose oxidase*	99.9%	NR	Morshed et al. (2019)
Paracetamol	Pharmaceuticals	*Horseradish peroxidase*	83.5%	7	Xu et al. (2015)
Bisphenol A	PEDCs	*Laccase*	90.0%	NR	Dai et al. (2016)
2,4,6-trichlorophenol	PEDCs	*Laccase*	85.0%	10	Xu et al. (2013)
Triclosan	PEDCs	*Laccase*	65.0%	NR	Xu et al. (2014)
Phenol	PEDCs	*Horseradish peroxidase*	29.68%	25	Temoçin et al. (2018)
Chlortetracycline	Pharmaceuticals	*Laccase*	58.3%	7	Taheran et al. (2017)
Pentachlorophenol	PEDCs	*Horseradish peroxidase*	83.0%	8	Niu et al. (2013)
Bisphenol A, Triclosan and 2,4-dichlorophenol	PEDCs	*Laccase*	92.6–99.7%	10	Dai et al. (2016)
Methyl orange	Dyes	*Horseradish peroxidase*	98.0%	10	Arslan (2011)
Naproxen, diclofenac	Pharmaceuticals	*Laccase*	90%	5	Zdarta et al. (2019)
2,4,6-trichlorophenol	PEDCs	*Laccase*	95.4%	7	Xu et al. (2017)
Catechol	PEDCs	*Laccase*	39.0% (COD)	NR	Wang et al. (2014)
Bisphenol A	PEDCs	*Tyrosinase*	80.0%	10	Zdarta et al. (2020)

Dyes or colorants are being extensively used in many industries such as textile, plastic, tannery, paper, pulp, electroplating, petroleum products, pharmaceutical, and cosmetic industries (Deb et al., 2019; Morshed et al., 2020). Many of these dyes that we are using on daily basis and releasing into surface water are made of complex aromatic compounds and often pose serious life-threatening consequences to living organisms if they came in contact (Nandi et al., 2009). They are resistant to conventional physical, chemical, and biological wastewater treatments such as coagulation, flocculation, adsorption, filtration, aerobic/anaerobic biological system, or a combination of the physical and biological system (Bernes 1998; Gaur et al., 2018). Therefore, special attention has been given to this avenue to explore new generation treatment methods. A number of reports has shown the potential of the heterogeneous enzymatic system using immobilized enzymes as green and resource-efficient process in the removal of toxic dyes and other contaminants from water (Karimi et al., 2012; Eskandarian et al., 2014; Aber et al., 2016; Ravi et al., 2020). (Arslan 2011) reported that immobilized *Horseradish peroxidase* is capable of sustainably remove 98% azo dyes from wastewater within 45 min. They have mentioned that the immobilized enzyme could be recycled 10 times while retaining 69.6% of its original activity (69.6% after 5 cycles and remained constant for another 5-repeated cycle) (Cristóvão et al., 2011). used cheap, easily available green coconut fiber for immobilization of commercial *laccase* and used them for removal of reactive dyes. They have studied the removal of a number of reactive dyes (individually and mixed). Their findings show as high as 90% removal of dyes when treated individually and 63% when dyes are mixed (Kahoush 2019). studied the removal of reactive dyes by using immobilized *glucose oxidase* enzyme on carbon felt through bio-Fenton and bio-electron Fenton system.

Pharmaceuticals are among the group of chemicals that are continually released into nature which ends up in wastewater. The chemicals are complex in nature and pose serious concern for both aquatic and human life. It is highly important to remove pharmaceutical residues from the wastewater. Removal of pharmaceuticals from wastewater by enzymes is being explored by many researchers, namely a few- (Taheran et al., 2017b) used covalently immobilized *laccase* onto Electrospun nanofibrous textile. They have reported the mineralization of commonly available pharmaceuticals (such as chlortetracycline, carbamazepine, and diclofenac) in wastewater. Results from their study demonstrated a successful 72.7%, 63.3%, and 48.6% degradation efficiency for chlortetracycline, carbamazepine, and diclofenac, respectively in 8 h of reaction. They have also reported that the resultant materials are reusable for up to 10 cycles. In another report (Taheran et al., 2017) have removed as high as 58.5% of chlortetracycline in a continuous system using immobilized *laccase* while retaining more than 50% of initial activity after 7 reuse cycles of the biocatalysts immobilized textile. From their experimental findings, they concluded that with the increase in flux rates the removal efficiency decreases. The best results were reported on the flux rate of 3 $mL/h \cdot cm^2$ (Gao et al., 2014). Reported that *organophosphate hydrolase* immobilized textile is capable of effective removal of readily available pesticides from wastewater. The results indicate that the resultant biocatalysts immobilized textiles can also be designed into a column reactor for continuous wastewater treatment application which is able to degrade the pollutants at high flow rates for over 60 days without a significant decrease in removal performance (Xu et al., 2015). Reported an advanced process by combining both the functionality of nanofiber textiles as an absorbent as well as the catalytic property of immobilized *horseradish peroxidase* for removal of toxic pollutants from wastewater. They immobilized *horseradish peroxidase* on poly (vinyl alcohol)/poly (acrylic acid)/SiO_2 electrospun nanofibrous textile. Results showed, 83.5% of paracetamol removal with excellent reusability up to 7 cycles while maintaining 40.6% of

enzyme initial activity. The nonlinear fitting results demonstrated that the kinetics of paracetamol removal followed the first-order reaction (Zdarta et al., 2019). used electrospun poly (L-lactic acid)-co-poly (ε-caprolactone) nanofibers textile as effective support for *laccase* immobilization, for removal of commonly used anti-inflammatories, naproxen, and diclofenac, which are present in wastewaters at environmentally relevant concentrations. They further reported that, given an optimal condition during the batch removal reaction, resultant biocatalysts immobilized textile is capable of removing 90% of both pharmaceuticals (having concentration as high as 1 mg $L^{-1)}$.

Phenolic endocrine-disrupting chemicals (PEDCs) have received extensive attention in recent decades in terms of their detections in environmental indicators, potential threats on human life and nature, and prospective removal from soil or water (Shakerian et al., 2020). Several researchers have also reported the application of biocatalysts immobilized textile for the removal of PEDCs from wastewater. For instance (Xu et al., 2013); reported that immobilized *laccase* can successfully remove >85% of 2,4,6-trichlorophenol from wastewater in an optimum reaction condition through a combined action of biodegradation/mineralization and adsorption. They have also found out that, the as-designed biocatalysts immobilized textile can be used for 10 cycles while retaining 50% of its original activity. Based on the studies of kinetics and mechanisms of pollutant removal they proposed that the high removal efficiency may be attributed to the combined effect of adsorption by Electrospun fibrous textile and enzymatic catalysis. In another attempt (Xu et al., 2017), they immobilized *laccase* on polyacrylonitrile/polyvinylidene fluoride nanofibrous textile for removal of 2,4,6-trichlorophenol (95.4% removal after 270 min) having appreciable reusability of 65.9% up to 7-cycles (Xu et al., 2014). further used *laccase* immobilized on mesoporous nanofibers textile for removal of triclosan (Wang et al., 2014). Reported the removal of catechol from wastewater through the combined effect of biocatalysis and adsorption using commercial *laccase* immobilized on polyacrylonitrile/montmorillonite/graphene oxide composite nanofibers textile. Dai, Yao, Song (Dai et al., 2016b), successfully encapsulated both multi-walled carbon nanotubes and *laccase* on electrospun nanofibrous membrane via emulsion electrospinning. They have reported that resultant material could remove 90% of widespread bisphenol A from wastewater in a wide range of pH, concentration, and temperature (Dai et al., 2016). also reported the fabrication of multi-walled carbon nanotube modified *laccase*-carrying electrospun fibrous membranes which is capable of widespread removal of phenolic organics from water, including bisphenol A (92.6 ± 0.74% removal), triclosan (95.5 ± 0.46% removal), and 2,4-dichlorophenol (99.7 ± 0.02% removal). They also reported that the resultant biocatalysts immobilized textile could be reused for 10 cycles without a significant decline in removal performance (Temoçin et al., 2018). covalently immobilized *horseradish peroxidase* on electrospun poly (vinyl alcohol)—polyacrylamide blend nanofibrous textile for removal of Phenol in real wastewater. They have reported that, the resultant material removed 29.68% phenol by 180 min providing 25-cycles reusability while retaining 54% of initial activity (Niu et al., 2013). encapsulated *horseradish peroxidase* into the nanofibrous textile by emulsion electrospinning to remove pentachlorophenol (83% removal) at room temperature (Zdarta et al., 2020). optimized the immobilization of *tyrosinase* immobilization through response surface methodology and used it for bio-catalytic removal of bisphenol A. They removed 80% of bisphenol A by 90 min of the process at 25 °C and pH 7. The optimized immobilization condition provided the additional stability and reusability of the *tyrosinase* upon immobilization: the immobilized enzyme retained around 90% of its initial activity after 30 days of storage, and was still capable to remove over 80% of bisphenol A even after 10 repeated uses.

By summarizing the above overview, biocatalyst immobilized textile has likely proved its potentiality in catalytic removal of various pollutants. Although this conclusion is very comforting, few serious drawbacks are yet to be addressed by the researchers before this technology can be used at an industrial scale, which includes; vulnerability to the surrounding environment; the necessity of pre-treatment of wastewater; poor performance in a system dealing with a mixture of pollutants. Tailoring the reactor, enzyme, support matrix and mass-transfer has been regarded as a prevalent quest to minimize or eliminate these drawbacks, which remains an open challenge to researchers in the field of textile biotechnology.

NR = not reported, PEDCs = Phenolic endocrine disrupting chemicals, COD = Chemical oxygen demand.

9. Challenges and future perspectives

Biocatalysts are often highly desired to catalyze various complex reactions in mild conditions. In this era of sustainability and green technology, their prospect and progress in different fields of application are growing exponentially. As discussed in this review, their immobilization process involves recyclability and reusability providing high stability and adequate activity that helps to better control the process and reduces the consumption of additional chemicals, energy, and time thus reducing the costs.

Despite all pros of immobilization of biocatalysts (enzymes), the process to immobilize biocatalyst on textiles is facing great challenges before it can be scaled-up. Various phenomena may lead to a total or partial loss of catalytic activity of the immobilized biocatalysts. Here are a few cases: (i) waste of enzyme during immobilization-almost all the studies reported the waste of enzyme during immobilization since not all enzymes are adsorbed by the textile or remain active after being adsorbed, (ii) enzyme leaching to media-while enzymes are bound to textile fiber surface through various bonds-reports show that a large quantity of enzymes gets leached away during application of the biocatalysts immobilized textile. Excessive leaching may create the necessity of removal of the enzyme from products, which might fail the whole idea for enzyme immobilization. (iii) blocking of active sites of enzymes. Inconvenient confrontation of enzymes on the textile surface may cause disorientated immobilization, which is undeniable for commercial application. (iv) interaction of the textile surface with immobilized enzyme-the surface of textile is not inherently neutral; therefore it is likely to interact with the immobilized enzyme and change the physicochemical properties of enzymes, lead to denaturation or poor affinity towards the substrates. (v) harsh conditions during immobilization-most of the immobilization involves specific conditional such a pH and temperature. Although most approaches have considered the ranges of optimum conditions for enzymes, yet undesired changes can lead to the loss of the folded 3D structure of the protein and the loss of the active site and activity of the enzyme as a whole. (vi) storage — biocatalysts reduce relative activity over time even in the most optimal conditions, which limits the potentiality of large-scale production and long-lasting application of “biocatalysts immobilized textile”. Besides them, there are challenges involving textile structure, modifications of textile surface, integration of favorable surface functional groups, and so on. Based on the literature studied in this review, the highest attention has been given to those challenges in this decade and considerable improvements have been made.

This whole concept of biocatalysts immobilized textile is fairly new and there are endless opportunities for improvement. To reduce the waste of enzymes during immobilization, resource-efficient processes such as printing can be considered as potential

solutions. Few approaches have already been introduced in enzyme printing, yet a detailed study based on various forms of the textile as well as various classes of the enzyme is yet to be done. Complex processes and harsh conditions used for the functionalization of textile fiber surfaces can be replaced with more resource-efficient and eco-friendly alternatives such as plasma treatment or bio-crosslinkers. All those possibilities can effectively improve the performance of biocatalysts immobilized textile and enhance its pervasive uses in wastewater treatment and various green chemistry applications.

Author contributions

All authors were involved in writing and revising the manuscript.

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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