Nanotechnology in Biofuels Production: A Novel Approach for Processing and Production of Bioenergy

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Abstract Now it's been well understood that only fossil fuel cannot meet our today's fuel need, and we have to have an alternative energy resource to keep our everyday activities going. Reportedly countries like USA, Brazil had tradition of using 'green plant': corn, sugar cane as renewable energy resource rather than non renewable source of energy like 'black fossil fuel', however an industrially applicable practice was required to keep environmental balance. Once researcher had understood the thermal processing of plants cellulosic biomass and lignin, followed by catalytic processing of formed biomass derived compound in liquid phase and catalytic conversion of final products, that practice had minimized health and environmental hazard in compared to when fossil fuel is burnt. Still a more cost effective source of fuel was necessary. Nanomaterials: carbon nano tubes (CNT), graphene, aluminum oxide were the answer. Once enzymes like laccase, lipase are immobilized, these could convert plant cellulose to sugar for repeated cycles of reactions, and produce a fuel without environmental hazards like green house effects.

Keywords Nano-biofuel · CNT · Aluminum oxide · Immobilization · Laccase

1 Introduction

We knew it since the last to last decade only that an alternative source of energy is required to meet the fuel appetite of developing human race. Researchers also were engaged to develop a newer, cheaper, and sustainable fuel resource. Since a long time ethanol has been used as an alternative source of fuel in the United States of America, using corn as 'green plant' source rather using 'black fossil fuel' like gasoline, diesel, or petrol (Balandrin et al. 1985). Whereas sugar cane was counted as a great energy source in Brazil. So it had been understood that, once a potential technology

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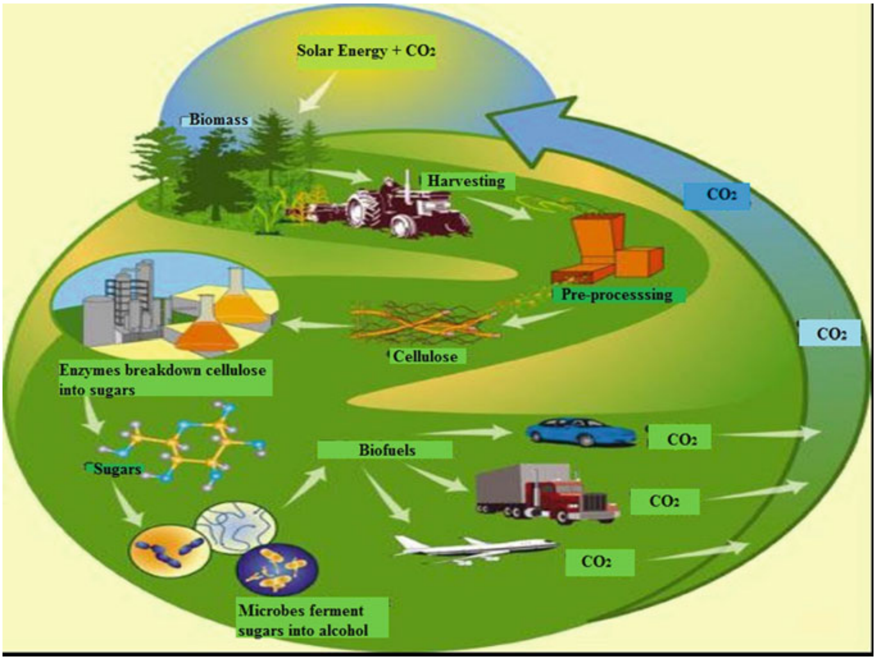

Fig. 1 Cycle of processing–production–usage of biofuel in today's life (Rao 2015)

is found to convert green plant's lignocelluloses (lignin and cellulose) to an economically and environmentally sustainable form of energy (Laborie 2009), that would be easily industrially applicable (Bharathiraja et al. 2014). Research was held mainly on issues like thermal processing of plants cellulosic biomass and lignin, followed by catalytic processing of formed biomass derived compound in liquid phase and finally catalytic conversion of final products and byproducts as well (Bartle and Myers 2001) to minimize health and environmental hazard in compared to produce when fossil fuel is burnt. Modern biotechnology and advanced knowledge of nanotechnology came up with the solution (Whitcombe et al. 2014). Once enzymes required for converting plant cellulose to sugar are immobilized with nanostructured materials (Gao et al. 2014), like multi-walled nanotubes, graphene, the enzymes are industrially used for repeated cycles of reactions, and produce a fuel without environmental hazards like green house effects, in the long run climate change as well. Another potential nanomaterial is aluminum oxide (Siepmann et al. 2008), which plays an important role in platinum/silica catalyst synthesis by strong electrostatic adsorption (SEA). Once in situ real-time tools to monitor catalytic chemistry in atomic scale are developed, like next-generation electron microscope, which would facilitate imaging nanosized chemical changes in aqueous medium, it would lead our footstep towards green environment (Fig. 1).

2 Different Biofuels Construction

Louisiana Tech Professors James Palmer, Yuri Lvov have showed that not only traditional fuel producing plants like sugar cane or corn; woods, grasses, agro wastes, but also household wastes could be considered as fuel source plant, due to their high cellulosic with a savings estimates ranging from approximately $32 million for each cellulosic ethanol plant, because of its reusability.

3 Role of Enzyme in Biofuel Fabrication

Enzymes are used in biofuel production mainly in two stages, one is for hydrolysis of agro waste as pretreatment to produce fermented sugar and another is for trans-esterification while producing biodiesel from plants like Jatropha, algae, or other oil plants. The difficulty with handling of enzyme is their shelf life. Most of the enzymes have half life of few minutes to some hours, as an industrially applicable tool, which has to be increased (Wang et al. 2001) demonstrates that immobilization of enzyme with glass beads or nanostructures could increase that up to thousand times (Fig. 2, Tables 1 and 2).

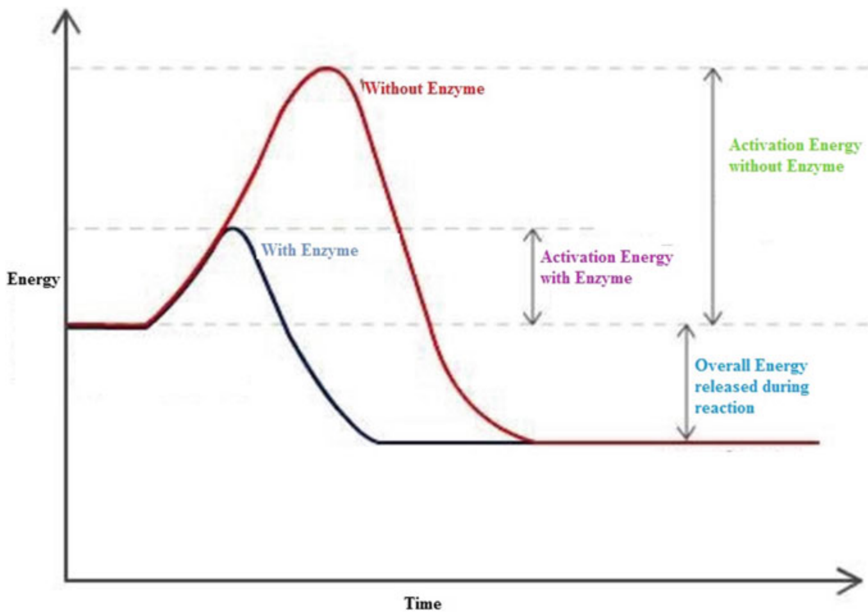

Fig. 2 Activation energy curve with and without enzyme

Table 1 Comparison of free enzyme and immobilized enzymes (Rao 2015)

Characteristics	Immobilized enzyme	Free enzyme
Cost	Low	High
Efficiency	High	Low
Stability	Stable	Unstable
Tolerance to temperature, pH	High	Low
Recovery	Possible	Not possible
Separation from substrate	Easy	Difficult
Separation from product	Easy	Difficult

Table 2 Comparison of different methods to immobilize enzyme (Rao 2015)

Method	Advantages	Disadvantages
Adsorption	Worked in mild condition, easy and low cost, weak interaction between lipase and the carrier make the immobilization, regenerated carrier for several times of usage	Lipase sensitive to pH, ionic strength, and temperature, the adsorption capacity is small and the protein might be stripped off from the carrier
Covalent bond	Thermally and operationally stable enzyme	The laborious preparation of immobilized enzyme might cause lipase to lose its activity, Some coupling reagents are toxic
Cross-linking	Lipase is stable due to the strong interaction between the lipase and the carrier	The cross-linking conditions are intense and the mechanical strength of the immobilized lipase is low
Entrapment	The conditions are moderate and applicable to a wide range of carrier and lipases, effective for low molecular weight substrates because it has the mass transfer restriction during the catalytic process, fast, cheap and easy	Difficulties raise while working with high molecular weight molecule

4 Function of Nanotechnology in Biofuel Processing Production

4.1 Fullerene

Fullerene is a molecule of carbon in the form of a hollow sphere, ellipsoid, tube, or in other shapes. Spherical fullerenes are also called Buckminsterfullerene (Bucky balls).

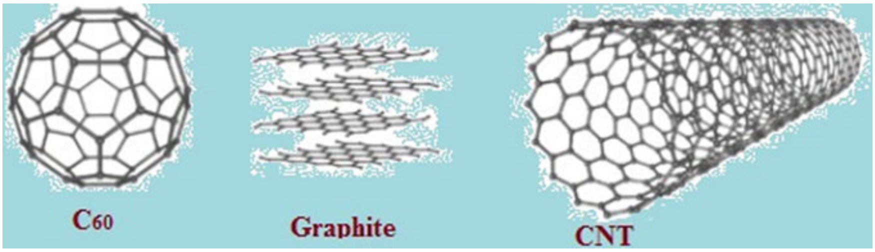

Fig. 3 Depicts different nanoclusters participating in immobilization of enzyme (Rao 2015)

Whereas cylindrical ones are called carbon nanotubes or bucky tubes. Fullerenes are similar in structure to graphite, which is composed of stacked graphene sheets of linked hexagonal rings, but they may also contain pentagonal (sometimes heptagonal) rings. The first fullerene molecule to be discovered, in family is namesake Buckminsterfullerene (C_{60}), was prepared by Richard Smalley, Robert Curl, James Health, Sean O' Brich, and Harold Kroto at Rice University. The name was homage to Buckminster Fuller, whose geodemic domes it resembles (Fig. 3).

4.1.1 Bucky Ball Cluster

Most common type of buckyball is C_{60}. Initially, carbon has only two allotropes, diamond and graphite. Once buckminsterfullerene was discovered, it became the smallest fullerene molecule containing pentagonal and hexagonal rings in which no two pentagons share an edge (which could destabilize the structure, as in pentalene). C_{36}, C_{70}, C_{76}, C_{84} buckyballs are new buckyballs of carbon participating in enzyme immobilization.

4.1.2 Carbon Nanotubes

Carbon atom can form long cylindrical tubes, also known as buckytubes. It is very much possible to make a buckytube with only single atomic layer thick = 1/50,000th that is the thickness of human hair.

Single-Walled Carbon Nanotube

Most single-walled nanotubes (SWNTs) have a diameter of close to one nanometer, and can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene sheet is wrapped and is represented by a pair of indices (n,m). The integers n and m denote the numbers of unit vectors along two directions in the honeycomb crystal lattice of graphene. If $m = 0$, the nanotubes is called zigzag nanotube. If $n = m$, the nanotube is called armchair nanotube, otherwise they are called chiral nanotube.

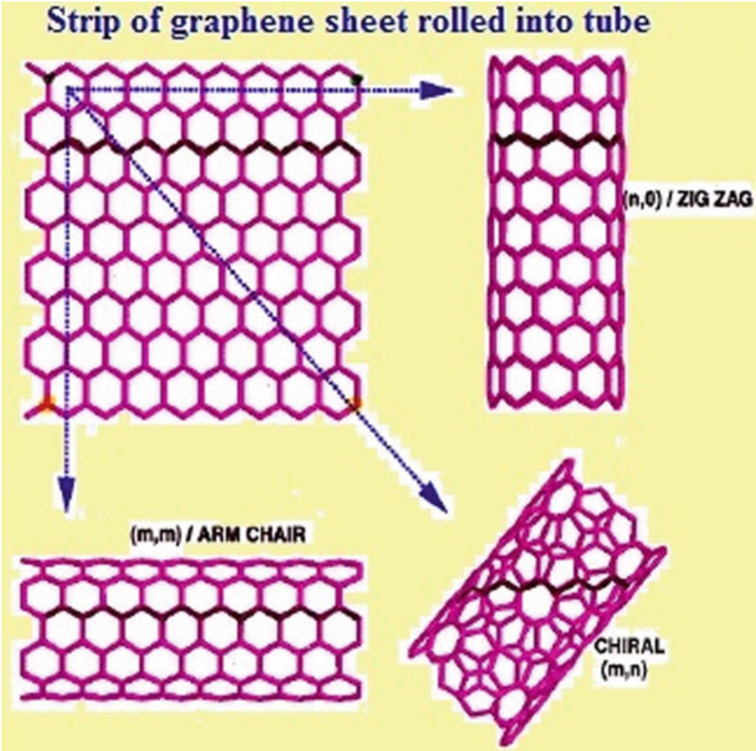

Fig. 4 Different conformations of graphene

Multi-walled Carbon Nanotube

Multi-walled carbon nanotube (MWNTs) consists of multiple rolled layers (concentric tubes) of graphene. These are two models that can be used to describe the structure of multi-walled nanotubes (Fig. 4).

4.2 Aluminum Oxide

Aluminum oxide is another potential nanomaterial used in immobilization of enzymes used in the biofuel production. It participates in the synthesis of platinum/silica catalyst through strong electrostatic adsorption (SEA), and moderates the loading capacity of immobilized enzyme.

5 Blending up Nano-Based Enzyme Models in Biofuel Production

5.1 Reasons Behind Change in Properties Once Immobilized with Nanomaterials

Using nanomaterials in biofuel processing production has twofold advantages. First and foremost is that nanomaterial increases the surface-to-volume ratio (SA:V); hence we end with an enzyme with high loading capacity (Mathew et al. 2009). And the dominance of quantum effects stabilizes the enzyme (Figs. 5 and 6).

5.2 Laccase

Laccase is an external enzyme, produced by various bacteria and fungi. This enzyme is mainly used in second-generation biofuel production (Madhavi and Lele 2009), for pretreatment of agro waste (Pawliszyn 1999), which degrades cellulosic compounds and sugar; and phenolics compounds are formed (Xu et al. 2015). Research has showed immobilization with nanomaterials, such as fullerene (C_{60}), multi-walled carbon nanotubes (MWNTs), oxidized-MWNTs (O-MWNTs), and graphene oxide

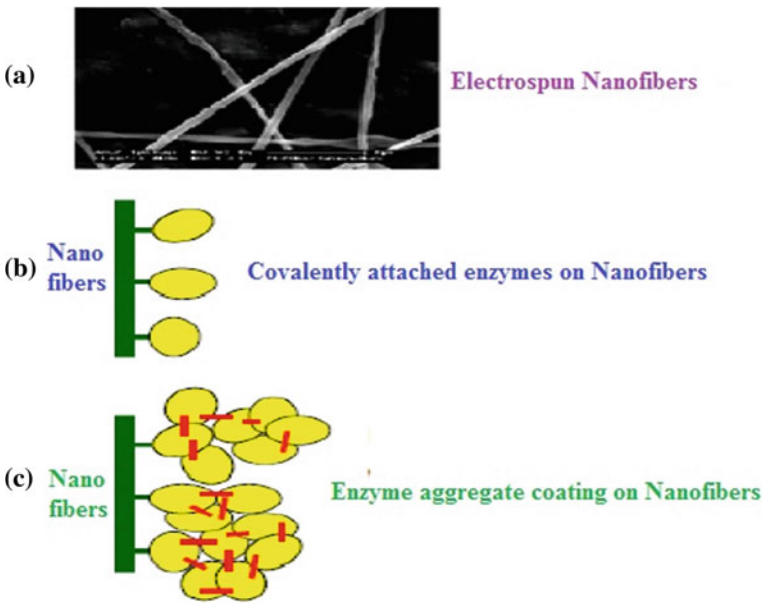

Fig. 5 Different techniques of enzyme immobilization; **a** Electrospun method, **b** Covalently attached, **c** Enzyme aggregate coatings (Rao 2015)

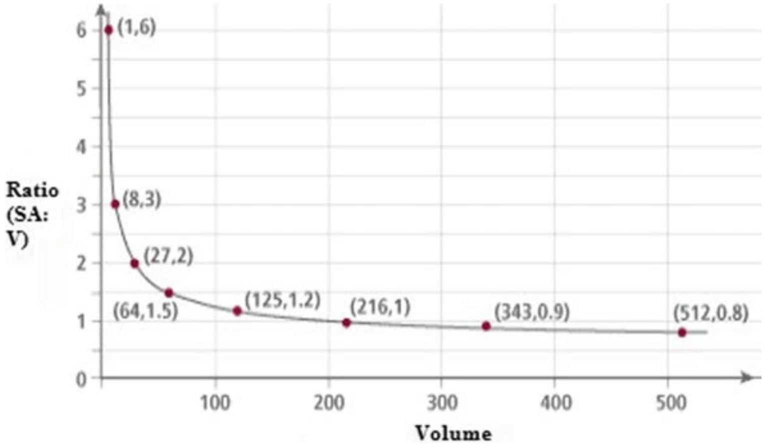

Fig. 6 Curve depicts the change of SA:V with change in volume, after conjugation with nanomaterials

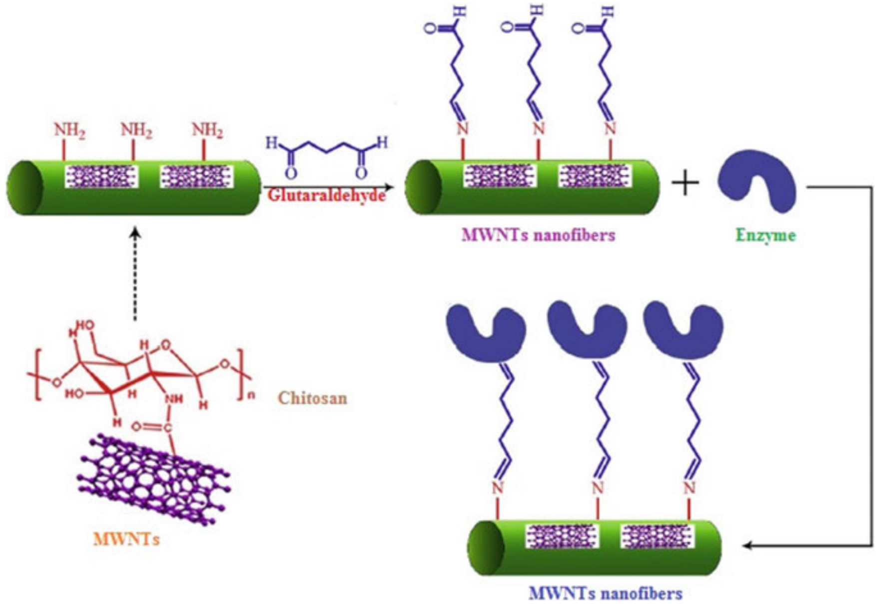

Fig. 7 Schematic demonstration of laccase enzyme immobilization via activation on MWNTs nanofiber membrane (Rao 2015)

(GO) increases the half life of laccase and stabilize it as well (Yücel et al. 2012). Here, O-MWNTs show the maximum loading capacity for enzyme laccase, whereas C_{60} demonstrates the lowest (Fig. 7).

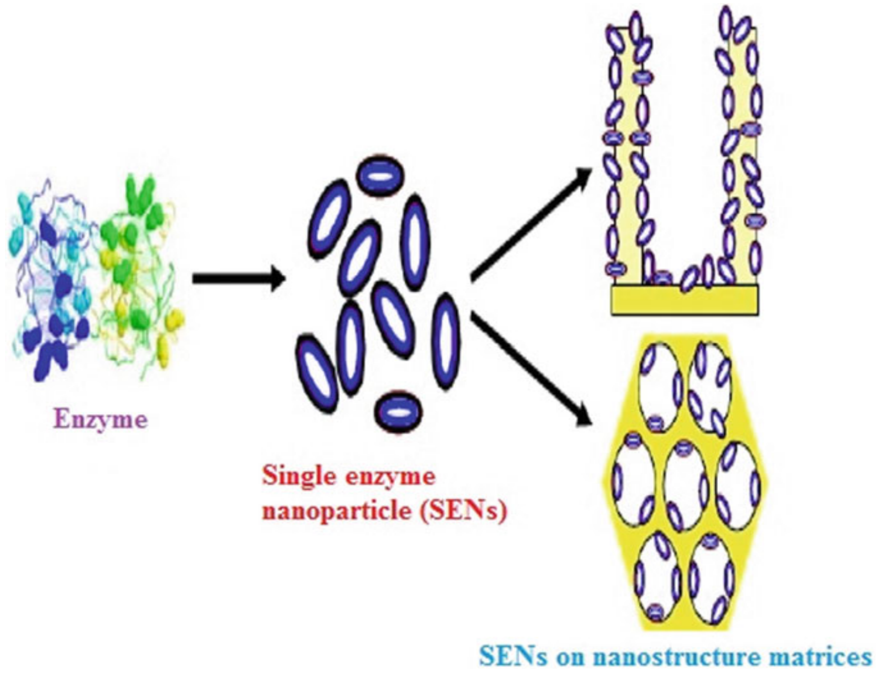

Fig. 8 Immobilization of SENs

5.3 Lipase

Biodiesel is usually known as methyl (or ethyl) esters of fatty acids obtained by trans-esterification (alcoholysis) of triglycerides. Lipase an extracellular or intracellular enzyme, obtained from fungi are immobilized in biomass support particles and used as catalytic beds to obtain prolong use (Yücel et al. 2012) (Fig. 8).

6 Conclusion

Nanotechnology plays a significant role in biofuel production, by assisting the immobilization of enzymes like laccase or lipase. As nanostructured enzyme has high surface area compared to free enzymes, immobilized enzymes have increased the shelf life or reusability up to thousand times. Though there is a limitation of enzymes with inhibitors, nanostructured immobilized enzyme shows equivalent catalytic activity when compared to free enzyme.

References

Balandrin MF, Kjocke AJ, Wurtele E et al (1985) Natural plant chemicals: sources of industrial and mechanical materials. Science 228:1154–1160

Bartle KD, Myers P (eds) (2001) Capillary electrochromatography. University of Leeds, UK

Bharathiraja B et al (2014) Biodiesel production using chemical and biological methods—a review of process, catalyst, acyl acceptor, source and process variables. Renew Sustain Energy Rev 38:368–382

Cserháti T, Forgács E (2003) Cyclodextrins in chromatography. Hungarian Academy of Sciences, Budapest, Hungary

Cywinski PJ, Moro AJ, Mohr GJ, Kutner K (2010) Chemosensors based on molecularly imprinted polymers. In: Topics in current chemistry. Springer, Berlin–Heidelberg

Dyson N (1998) Chromatographic integration methods, 2nd edn. Dyson Instruments, UK

Future applications of nanotechnology, Trade News Singapore

Gao W, Huang H, Shi H, Feng X, Song W (2014). Nitrogen-rich graphene from small molecules as high performance anode material. *Nanotechnology* 25:415402

Guo F et al (2012) Solid acid mediated hydrolysis of biomass for producing biofuels. Prog Energy and Combust Sci 38(5):672–690

Hanai T (2000) HPLC: a practical guide. Health Research Foundation, Kyoto, Japan

Hanna R, Maciej JN, Lapinsky L, Adamowicz L (1998) Molecular structure and infra red spectra of 2-hydroxy-1, 4-naphthaquinone; Experimental matrix isolation and theoretical Hartree-Fock and post Hartree-Fock study. Spec Act 54: 1091–1103

Johnston CT (2010) Probing the nanoscale architecture of clay minerals. Clay Miner 45:245–279

Kim J, Jia H, Wang P (2006) Challenges in biocatalysis for enzyme-based biofuel cells. Biotechnol Adv 24(3):296–308

Laborie MP (2009) Chapter 9. Bacterial cellulose and its polymeric nanocomposites. In: Lucia L, Rojas O (eds) The nanoscience and technology of renewable biomaterials. Blackwell Publishing, Hoboken

Lapshin RV (2011) Feature-oriented scanning probe microscopy. In: Nalwa HS (ed) Encyclopedia of Nanoscience and Nanotechnology. American Scientific Publishers, USA, pp 105–115

Madhavi V, Lele SS (2009) Laccase: properties and applications. BioResources 4(4):1694–1717

Mathew AP, Laborie M-P, Oksman K (2009) Cross-linked chitosan-chitin whiskers nanocomposites with improved permeation selectivity and pH stability. Biomacromolecules 10(6):1627–1632

Mehta CM (2012) Role of microbiologically rich compost in reducing Biotic and abiotic stresses. Microorganisms in Environmental Management

Mukhopadhyay A, Dasgupta AK, Chakrabarti K (2014) Enhanced functionality and stabilization of a cold active laccase using nanotechnology based activation-immobilization. Bioresource Technology

Noraini MY et al (2014) A review on potential enzymatic reaction for biofuel production from algae. Renew Sustain Energy Rev 39:24–34

Pang R, Li M, Zhang C (2015) Degradation of phenolic compounds by laccase immobilized on carbon nanomaterials: diffusional limitation investigation. Talanta 131:38–45

Pavlidis IV et al (2012) Development of effective nanobiocatalytic systems through the immobilization of hydrolases on functionalized carbon-based nanomaterials. Bioresour Technol 115: 164–171

Pawliszyn J (ed) (1999) Applications of solid phase microextraction. University of Waterloo, Waterloo, Ontario, Canada

Putzbach W, Ronkainen NJ (2013) Immobilization techniques in the fabrication of nanomaterial-based electrochemical biosensors: a review. Sensors 13(4):4811–4840

Rao A (2015) Nanotechnology: Applications in biofuel productions. Conference paper, VIT University, January 2015 (https://www.reserachgate.net/publication/271902586)

Shen Y (2014) Carbon dioxide bio-fixation and wastewater treatment via algae photochemical synthesis for biofuels production. RSC Adv 4(91):49672–49722

Siepmann F, Siepmann J, Walther M, MacRae RJ, Bodmeier R (2008) Polymer blends for controlled release coatings. J Controlled Release 125:1–15
Szpunar J, Lobinski R (eds) (2003) Hyphenated techniques in speciation analysis. CNRS, Pau, France
Whitcombe MJ, Kirsch N, Nicholls IA (2014) Molecular imprinting science and technology: a survey of the literature for the years from 2004 to 2011. J Mol 27:297–401
Xu R et al (2015) Enhancement of catalytic activity of immobilized laccase for diclofenac biodegradation by carbon nanotubes. Chem Eng J 262:88–95
Yücel S, Terzioğlu P, Özçimen D (2012) Lipase applications in biodiesel production