Biosurfactant-Aided Bioprocessing: Industrial Applications and Environmental Impact

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Abstract

Surfactants are classified as ionic, nonionic, and zwitterionic surfactants based on the ionic properties of the polar head group. Biosurfactants are surface-active compounds produced by microbes, possessing both hydrophilic and hydrophobic moieties. In biosurfactants, the lipophilic moiety is generally a protein or peptide with a high fraction of hydrophobic side chains or a hydrocarbon chain of a fatty acid with 10 to 18 carbon atoms, whereas the hydrophilic moiety is an ester; hydroxyl, phosphate, and carboxylate group; or sugar. Biosurfactants have specific advantages over chemical surfactants, such as biodegradable and environmental-friendly nature, production at lower temperatures, effectiveness at low concentrations, low toxicity, high selectivity because of the presence of specific functional groups, and efficiency to work at extreme environmental conditions of temperatures, pH, and salinity, rendering them suitable for different industrial applications. However, large-scale commercial application of biosurfactants is impeded because of their high production costs, ineffective bioprocessing methods, less efficient microbial strains, and the exorbitant downstream processing costs. Biosurfactants find potential industrial application in areas, such as disruption of cell biomass, hydrocarbon bioremediation, and heavy metal bioremediation. Different groups of microbes, such as bacteria, yeasts, fungi, and actinomycetes are capable of producing biosurfactants. Some of the extensively studied biosurfactant producing microbial genera include *Pseudomonas,*

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Acinetobacter, Bacillus, Candida and *Torulopsis*. Development of improved and cost-efficient application technologies coupled with genetic engineering and strain improvement techniques and improved production processes will help in large-scale application of biosurfactants in the near future.

Keywords
Biosurfactants • Bioprocessing • Bioremediation • Lignocellulosic biomass • Production cost • Rhamnolipids • Sophorolipids

3.1 Introduction

Bioprocess employs complete living cells (microbes) or their metabolites (enzymes) for getting the desired end product. Industrial biotechnology deals with the application of biotechnological tools in different industrial processes, including bioprocessing and production of value-added products from renewable feedstocks. Manipulation of microbes and their physiology through the application of genetic engineering tools facilitates the development of new and cost-effective, cleaner, and environmentally friendly industrial manufacturing processes. Substantial amount of biomass generated from different agro-processing industries is not being commercially exploited, because of lack of infrastructure for collection, handling, and management of such a biomass. Despite being rich in nutrients, this valuable biomass is burnt leading to environmental pollution problems and loss of important rich resource. Thus, this enormous biomass considered as "waste" possesses great potential to be converted into a great variety of value-added products, such as biofuels, animal feeds, and human nutrients, which besides mitigating the greenhouse effect and atmospheric pollution problems is likely to help in better biomass management (Pothiraj et al. 2006).

According to a recent survey, global consumption of oil rose from 1.1 in 2014 to 1.9 million barrels per day (b/d) in 2016 (BP Statistical Review of World Energy 2016). In addition to the rising global oil demand, there are growing concerns about diminishing known petroleum reserves and the adverse effects of atmospheric greenhouse gases (GHG). This has resulted in search for alternative sources of energy and renewed interest in the production of fuels from plants or organic wastes, termed as "biofuels."

Biofuels mainly derived from food crops, such as corn, sugarcane, soybean, vegetable oil, etc., are regarded as "first-generation biofuels." In addition to their potential of being used after blending with petroleum-based fuels, they face many challenges including food-versus-fuel debate resulting in hike in food prices, production of food crops leading to change in land use pattern, and potential increase in GHG emissions. Moreover, the economic feasibility of the processes implied for first-generation biofuel production is based on the type of feedstock and the area of cultivation of that particular feedstock (Naqvi and Yan 2015). Therefore,

Table 3.1 Comparison of merits and demerits of first- and second-generation biofuel and petroleum fuels

	Petroleum refinery	First-generation biofuels	Second-generation biofuels
Feedstocks	Crude petroleum	Food crops, vegetable oils, corn sugar, etc.	Agricultural and forest residues
Products	Diesel, kerosene, jet fuel	Biodiesel, corn ethanol, etc.	Bio-oil, ethanol, butanol, mixed alcohols, etc.
Benefits	Major fuel	Environment friendly	Environment friendly
		Economic and social security	Nonfood cheap, abundant biomass
			Grown on marginal lands
Demerits	Expensive technology	Expensive technology	Efficient technology, development is still under progress
	Nonrenewable sources	Significant of land requirement	Renewable source

second-generation biofuels largely produced from lignocellulosic biomass are cheap and abundantly available as nonfood materials which offer a potential alternative to meet the growing global fuel demands. In addition, second-generation biofuels also provide several benefits to the society, such that they (i) are renewable and sustainable, (ii) help to mitigate the greenhouse gases (GHG) emission in the atmosphere, (iii) facilitate development of local economy through creation of job opportunities, (iv) reduce air pollution caused by burning or rotting of biomass in fields, and (v) ensure energy security for countries dependent on oil being imported from the other countries (Greenwell et al. 2012; Lee and Lavoie 2013). Comparison on advantages and disadvantages of the first-generation biofuels, petroleum fuels, and second-generation biofuels is presented in Table 3.1 which corroborates the importance of the second-generation biofuels.

There are two routes for converting biomass to biofuels: "thermochemical" route, commonly known as biomass-to-liquid (BTL) conversion process, and the "biochemical" route. In the case of BTL, the biomass is subjected to pyrolysis or gasification to generate syngas (composed of carbon monoxide and hydrogen) which is subsequently converted to fuels using either a catalytic process, such as the Fischer-Tropsch reactions, or by a biological conversion method (Balan 2014). In "biochemical" route, holocellulose content (cellulose and hemicellulose) available in the biomass is converted to monomeric sugars, which can be further utilized for the production of valuable compounds, like fuels, organic acids, etc. It is estimated that in economic terms, second-generation biofuel production processes are two to three times more expensive than the petroleum fuels on an energy-equivalent basis and over five times that of similar capacity first-generation bioethanol plants (Wright and Brown 2007; Carriquiry et al. 2011). Several challenges in the areas of bioprocessing of feedstocks, such as feedstock production and logistics, development of energy-efficient technologies for pretreatment and enzymatic hydrolysis of biomass, upstream and downstream processing cost, biofuel distribution, its acceptance in the society, and environmental impacts, need to be addressed to alleviate the fears and to lower down the production costs of the second-generation biofuels (Luo et al. 2010; Menon and Rao 2012).

A consortium of hydrolytic enzymes known as molecular scissors is required to cleave the complex network of cellulose, hemicellulose, and lignin in the lignocellulosic biomass to produce specific monomeric sugars (Zhang et al. 2012). Lower enzyme quantity and enzyme efficiency and higher enzyme costs required to hydrolyze lignocellulosic biomass are the limiting factors in bioprocessing applications. In the recent years, companies manufacturing enzymes commercially have made significant progress in overcoming these problems using different biotechnological and process engineering approaches (Alvira et al. 2013). Development of an efficient and potent process for production of ethanol as a liquid fuel after conversion of cellulose in the lignocellulosic biomass depends on many factors, such as lignin content in biomass, pretreatment effectiveness, cellulose crystallinity, substrate concentration, and productive hydrolysis of cellulose into monomeric units (Jeoh et al. 2007; Hall et al. 2010; Zeng et al. 2014). Moreover, high enzyme concentrations are needed to achieve efficient hydrolysis of biomass, thereby increasing the processing costs. The major difficulties surface up during the recycling of enzymes adsorbed on the residual lignocellulosic material. Thus, different ways to enhance the enzyme efficacy are required to reduce their consumption during hydrolysis, maintaining higher sugar productivity.

Surfactants are amphiphilic surface-active agents having both hydrophilic as well as hydrophobic entities that lessen surface tension between two immiscible fluids after accumulating at their interface (Fig. 3.1). The term “Surfactants” was created and registered as a trademark for the first time by the General Aniline and Film Corp for their surface-active products (GAF 1950; Schramm et al. 2003) and was later released in the public domain (Stevens 1969).

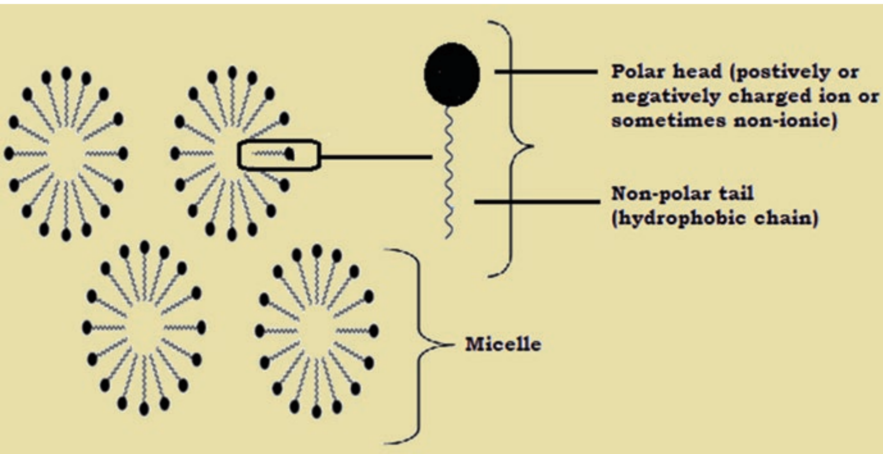


Fig. 3.1 Structure of several surfactant molecules forming micelles

Table 3.2 List of global biosurfactant manufacturers

S. No.	Name of the manufacturer	Biosurfactant manufactured
1	Kao Co Ltd., Japan	Sophorolipids
2	Iwata Chemical Co. Ltd., Japan	Rhamnolipids
3	Wako Pure Chemical Industries, USA	Surfactin
4	MG Intobio Co. Ltd., South Korea	Rhamnolipids
5	Jeneil Biosurfactant Company, USA	
6	Groupe Soliance, France	Sophorolipids
7	Ecover, Belgium	Sophorolipids
8	AGAE Technologies LLC, USA	Rhamnolipids
9	Apollo Biolife, India	Sophorolipids

Surfactants can either be of synthetic origin or biological origin (biosurfactants). Biosurfactants present an edge over chemical surfactants due to their numerous advantages, such as biodegradable and environment-friendly nature, production at lower temperatures, effectiveness at low concentrations, low toxicity, high selectivity because of the presence of specific functional groups, and efficiency to work at extreme environmental conditions of temperatures, pH, and salinity, which renders them suitable for different industrial applications (Kapadia and Yagnik 2013; Santos et al. 2013). However, their large-scale commercial application is hindered due to their high production costs, ineffective methods of bioprocessing, less efficient microbial strains, and the exorbitant downstream processing costs (Marchant and Banat 2012; Campos et al. 2013; Banat et al. 2014). Although, there is a restricted commercial production of biosurfactants due to huge production cost and low yields, in the recent times, new microbial strains and process interventions have helped in improving their productivity by 10–20-fold. Some of the companies manufacturing different types of biosurfactants are listed in Table 3.2.

Due to their important characteristics, surfactants are in high demand for bioprocessing applications (Saharan et al. 2011). This is largely because of the increasing interest in surfactant-aided hydrolysis of cellulose (Hseih et al. 2015; Min et al. 2015; Li et al. 2016). Different mechanisms, such as surfactant adsorption on air-liquid interface preventing enzyme denaturation, increase in available cellulose surface, and/or removal of inhibitory lignin, have been suggested for efficient enzymatic hydrolysis of cellulose (Min et al. 2015; Li et al. 2016). Based on kinetic analysis, surfactants can also increase the availability of reaction sites, leading to enhanced hydrolysis rate (Samiey et al. 2014).

Therefore, the aim of this chapter is to provide an insight into various possible mechanisms for action of biosurfactants and their application in bioprocessing along with their futuristic potential. Information presented in the chapter also provides an insight into the development of an efficient bioprocess for conversion of lignocellulose into biofuel and sets a platform for research on biosurfactant-aided pretreatment and hydrolysis for production of second-generation bioethanol from lignocellulosic biomass.

3.2 Surfactants and Their Classification

Surfactants are characteristic organic compounds, possessing both water-insoluble hydrophobic groups (tails) and water-soluble hydrophilic groups (heads) that decrease the surface tension at the interface of two liquids or liquid and solid (Saharan et al. 2011). Surfactants have diverse industrial applications, such as in food processing industries, agrochemical and pharmaceutical products, personal care and laundry products, petroleum, fuel additives, lubricants, paints, coatings and adhesives, photographic films, biological systems and various medical practices, soil remediation techniques, and also other environment-friendly methods (Schramm et al. 2003; Mishra et al. 2009).

It is estimated that during 2015–2020, world consumption of surfactants will continue to expand at an average annual rate of 1–5% (IHS 2016). Global surfactant market is calculated to grow by value at a compound annual growth rate (CAGR) of 5.5% and is predicted to reach a volume of 24,037.3 KT corresponding to $42,120.4 million in monetary terms by 2020. In terms of volumes, the anionic surfactants ruled the global market, with 7686.1 KT, followed by the nonionic surfactants at 6345.7 KT in 2014. Additionally, share of the amphoteric surfactants that represent 7.2% of the global surfactant market in 2014 is predicted to rise at the highest CAGR in the duration of 2015–2020 (www.marketsandmarkets.com/Market-Reports/biosurfactants-market-493.html).

On the basis of the ionic properties of the polar head group, surfactants are categorized into different groups, such as ionic (anionic and cationic), nonionic, and zwitterionic. Cationic surfactants carry a positive charge; on the other hand, a negative charge is present on the polar head groups of anionic surfactants. Zwitterionic or amphoteric surfactants possess both positive and negative charges depending on the environment in which they are present, whereas nonionic surfactants do not carry any charge on their head groups (Fig. 3.2). Different classes of surfactants with examples and their structures are presented in Table 3.3.

3.3 Ionic (Anionic and Cationic) Surfactants

Anionic surfactants get dissociated in water as an amphiphilic anion, which acts as surface-active portion of the molecule and a cation, which is generally an alkaline metal (Na^+, K^+) or a quaternary ammonium ion (Salager 2002). The commonly used anionic surfactants in various industrial applications are (a) carboxylates (alkyl carboxylates-fatty acid salts), (b) sulfates (alkyl sulfates, alkyl ether sulfates), (c) sulfonates: docusates (dioctyl sodium sulfosuccinate, alkyl benzene sulfonates), and (d) phosphate esters (alkyl-aryl ether phosphates; alkyl ether phosphates). These are also employed in pharmaceutical and cosmetic industries. For example, sodium lauryl sulfate BP containing sodium dodecyl sulfate with bacteriostatic action against gram-positive bacteria is applied as a skin cleaner and also a component in the medicated shampoos (Mishra et al. 2009; Sekhon 2013; Azarmi and Ashjaran 2015).

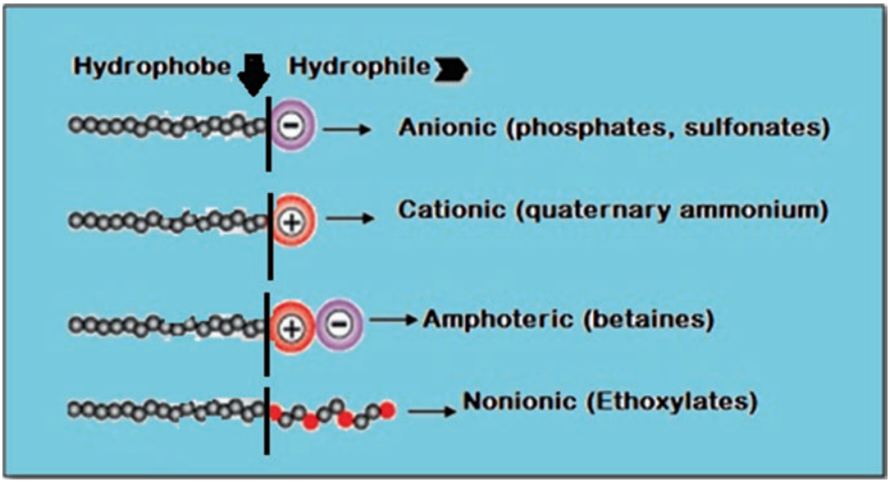


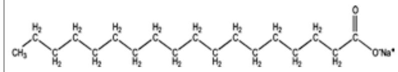
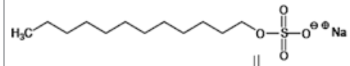
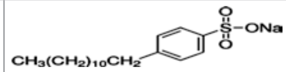
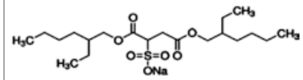
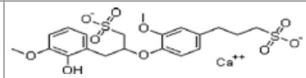
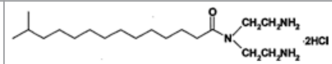
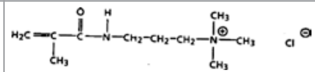
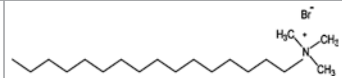
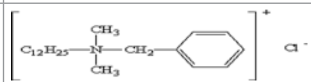
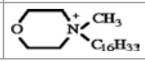
Fig. 3.2 Types of surfactants on the basis of polarity of head group

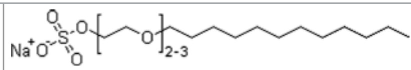
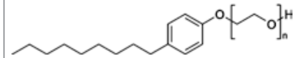
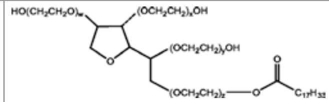
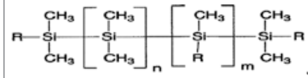
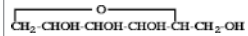
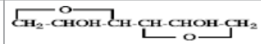
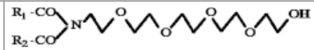
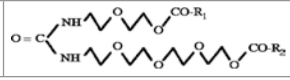
Cationic surfactants segregate in aqueous solution into a surface-active amphiphilic cation and an anion (mostly halogen type). Cationic surfactants majorly constitute a huge fraction of nitrogenous compounds, like amine and quaternary ammonium salts with one or many long alkyl chains originating from natural fatty acids (Salager 2002). Due to their positive charge, they adsorb strongly on negatively charged solid surfaces imparting special characteristics, like anti-caking, corrosion inhibition, dispersion, germicidal action, etc., to the substrates. These also have property to destroy a wide range of gram-positive and some gram-negative microbes. Such surfactants find application in cleansing wounds or burns on the skin (Mishra et al. 2009; Azarmi and Ashjaran 2015). The most widely used surfactants in this category are "Esterquats" with ester bonds which are generally more expensive than anionics and nonionics, because their synthesis involves high-pressure hydrogenation reactions. However, these surfactants show poor detergency (Sekhon 2013).

3.4 Nonionic Surfactants

Nonionic surfactants do not dissociate in water due to the non-dissociable nature of their hydrophilic group, such as alcohol, phenol, ether, ester, or amide, and are compatible with all other types of surfactants (Salager 2002). These can be described as polyolesters, polyoxyethylene esters, poloxamers polyolesters including glycol, glycerol esters, and sorbitan derivatives. Fatty acid esters of sorbitan (commonly known as Spans, e.g., Span 40, Span 60, Span 80, etc.) and their ethoxylated derivatives (frequently referred to as Tweens, e.g., Tween 20, Tween 40, Tween 80) are one of the most commonly used nonionic surfactants. Polyoxyethylenated mercaptans have slight unpleasant odor. The most repeatedly used surfactants in this group

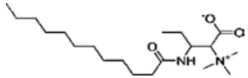
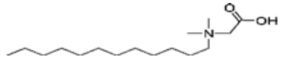
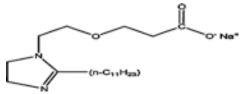
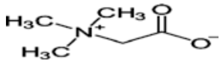
Table 3.3 Classification of surfactants on the basis of the nature of the polar head group

Class	Examples	Structures
Anionic	Sodium stearate	
	Sodium dodecyl sulfate	
	Sodium dodecylbenzenesulfonate	
	Dialkyl sulfosuccinate	
	Lignosulfonates	
Cationic	Laurylamine hydrochloride	
	Trimethyl dodecylammonium chloride	
	Cetyltrimethylammonium bromide	
	Benzalkonium-ammonium chloride	
	N,N-cetylmethyl morpholinium cation	

Nonionic	Polyoxyethylene alcohol	
	Alkylphenol ethoxylate	
	Polysorbate 80	
	Propylene oxide-modified polydimethylsiloxane	
	1-5 sorbitan	
	1-4,3-6 isosorbitan	
	Ethoxylated imide	
	Diacyl ethoxy urea	

(continued)

Table 3.3 (continued)

Class	Examples	Structures
Zwitterionic	Lauramidopropyl betaine	
	Dodecyl betaine	
	Cocoamido-2-hydroxypropyl sulfobetaine	
	Trimethylglycine betaine	

are Polysorbate 20, Polysorbate 80, and Poloxamer 188 which are generally applied in a concentration ranging between 0.001 and 0.1% and mainly find their application as emulsifying agents, dispersants, and solubilizers in pharmaceutical industry (Abraham 2003). Nonionic surfactants are mostly used as gelling and foaming agents and also in the fabrication of several drugs and nano-carriers for drug delivery systems (Mishra et al. 2009; Azarmi and Ashjaran 2015; Carter and Puig-Sellart 2016). In the USA, the neutral agent nonoxynol-9 is commonly used as vaginal spermicide. However, octoxynol has also been approved by the Food and Drug Administration (FDA) to be used in contraceptives and other vaginal drug products (Sekhon 2013).

3.5 Zwitterionic (Amphoteric) Surfactants

Zwitterionic or amphoteric surfactants exhibit both positive and negative charges on the surface-active portion, for example, betaines or sulfobetaines and natural substances, like amino acids, phosphatidylcholine (lecithin), and phospholipids. These surfactants are very mild, compatible with all the other types of surfactants, and less irritating to the skin and eyes than the other types revealing excellent dermatological properties. Moreover, due to their high foaming potential and insolubility in most organic solvents, amphoteric surfactants are largely used in shampoos, cosmetic products, and hand dishwashing liquids (Mishra et al. 2009; Azarmi and Ashjaran 2015).

3.6 Biosurfactants

Microbially produced surface-active compounds, possessing both hydrophilic and hydrophobic moieties, are commonly referred to as biosurfactants (Kugler et al. 2015). In biosurfactants, the lipophilic moiety is generally a protein or peptide with a high fraction of hydrophobic side chains or a hydrocarbon chain of a fatty acid with 10 to 18 carbon atoms, whereas the hydrophilic moiety is an ester; hydroxyl, phosphate, and carboxylate group; or sugar (Campos et al. 2013). Biosurfactants are structurally diverse group of secondary metabolites secreted in liquid culture media by aerobic microorganisms requiring a carbon source, such as carbohydrates, hydrocarbons, fats, and oils, to perform vital roles for their metabolic processes (Silva et al. 2014). Biological surfactants help in the microbial growth by facilitating the availability of hydrocarbons to the microbes with increase in the area at the aqueous-hydrocarbon interfaces across their cell membranes, thereby enhancing utilization by microorganisms, and also help in protection of microbes from harsh environmental conditions (Aulwar and Awasthi 2016). These compounds have amphipathic molecules which act between solutions of different polarities reducing surface tension, thereby allowing access to the hydrophobic substrates due to enhanced contact area between insoluble compounds (such as hydrocarbons) resulting in their enhanced mobility, availability to living forms, and, thus, biodegradation of such

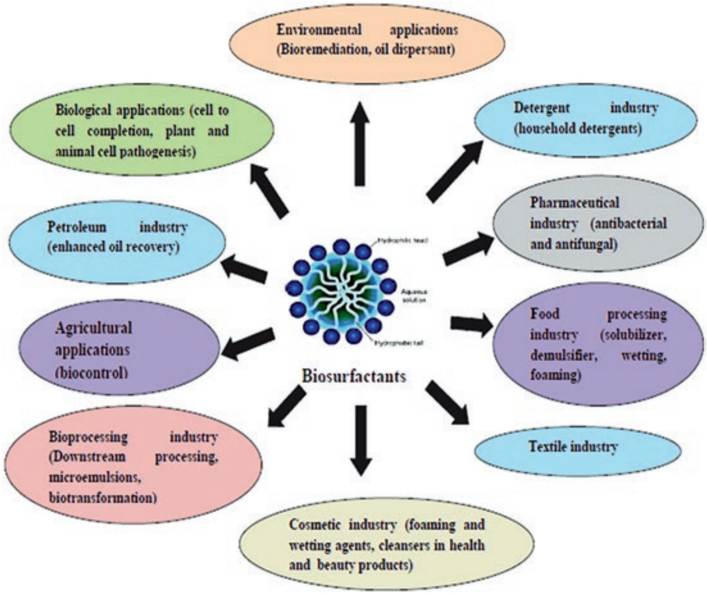


Fig. 3.3 Diverse industrial applications of biosurfactants

compounds (Arparna et al. 2011). Biosurfactants find diverse applications in a wide range of industries as mentioned previously (Banat et al. 2010; Marchant and Banat 2012; Campos et al. 2013; Lawniczak et al. 2013; Reis et al. 2013). A general outlay of various industrial applications of biosurfactants is presented in Fig. 3.3.

Due to the capabilities of biosurfactants for being used in diverse industrial processes, many patents have been granted in recent years involving biosurfactant production by different microbes, specifically *Pseudomonas* spp., *Acinetobacter* spp., *Bacillus* spp., *Candida* spp., and *Torulopsis* spp. (Sachdev and Cameotra 2013). Patents on the biosurfactant production by a consortium of microbes involving *Corynebacterium* spp., *Alcaligenes* spp., and *Methylomonas* spp. have also been filed (Shete et al. 2006; Rahman and Gakpe 2008).

3.7 Classification and Properties of Biosurfactants

Biosurfactants are generally divided into two classes, where class I contains low-molecular-mass molecules, such as glycolipids, lipopeptides, and phospholipids, which efficiently reduce surface and interfacial tensions, and class II comprises high-molecular-mass polymer agents including polymeric and particulate surfactants with effective emulsion-stabilizing properties (Kapadia and Yagnik 2013). Biosurfactants allow two immiscible phases to interact more readily by decreasing interfacial tension between the two dissimilar phases (Chavez and Maier 2011). Efficiency of biosurfactants is based on their concentration required to obtain the

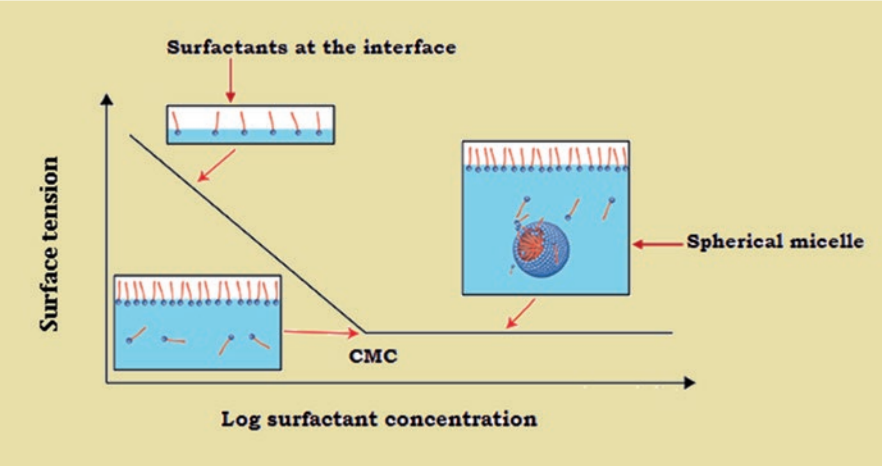


Fig. 3.4 Micelle formation in biosurfactants above critical micelle concentration (CMC)

critical micelle concentration (CMC). It is noteworthy to mention here that biosurfactant molecules aggregate at concentrations above the CMC to form micelles which further enable them to lessen the surface and interfacial tension resulting in enhanced solubility and bioavailability of otherwise reluctant hydrophobic organic compounds (Fig. 3.4). Therefore, critical micelle concentration is inversely related to the efficiency of biosurfactants, which implies that less biosurfactant concentration is needed to reduce the surface tension (Desai and Banat 1997). In standard terms, an effective biosurfactant can lower down the surface tension of water from 72 to 30 mN per meter and the interfacial tension between water and n-hexadecane from 40 to 1 mN per meter.

Biosurfactants are representative amphiphilic biomolecules that contain both hydrophilic and lipophilic groups. The hydrophile-lipophile balance (HLB) number is used to calculate the ratio of these groups, and its value between 0 and 60 defines the affinity of a surfactant for water or oil. Emulsifiers with low HLB are lipophilic and stabilize water-in-oil emulsification, while the emulsifiers with high HLB are hydrophilic (Desai and Banat 1997; Christofi and Ivshina 2002). HLB numbers calculated for nonionic surfactants are in the range from 0 to 20 wherein surfactants with HLB numbers > 10 possess affinity for water (hydrophilic) and HLB numbers < 10 show affinity toward oil (lipophilic). Recently, ionic surfactants have also been assigned HLB values extending above the value of 60 (Sajjadi et al. 2003). Thus, biosurfactant effectiveness can be estimated by its capability to minimize surface and interfacial tensions, by stabilization of emulsions, and also by measuring its hydrophilic-lipophilic balance (HLB).

3.8 Microbes Used for Production of Biosurfactants

A variety of microorganisms including bacteria, fungi, and yeasts can produce biosurfactants as mentioned in Table 3.4. Bacteria mainly belonging to the genus *Pseudomonas* and *Bacillus* are major bacteria known to produce significant amount of rhamnolipids and lipopeptide biosurfactants, while yeasts belonging to the genus *Candida* are efficient producers of rhamnolipids and lipopeptide biosurfactants (Arparna et al. 2011; Al-Bhary et al. 2013; Campos et al. 2013).

Because of the important diverse applications, the economics of biosurfactant production draws increasing attention worldwide. Moreover, due to emerging focus on sustainability and environmental impacts, industrial focus is shifting from the chemical surfactants to biosurfactants, but as mentioned previously, their high production cost is a major deterrent. During the past decade, substantial increase in the global biosurfactant production has been observed which is evident from the fact that in 2013, biosurfactant production was about 344,068 tons, but at a current compound annual growth rate (CAGR) of 4.3%, it is speculated to reach up to 476,512 tons by 2018 (Transparency Market Research 2014). Thus, there is an urgent need to develop new strategies for commercial production of biosurfactants through improved biotechnological processes. Two basic approaches are adopted globally for cost-efficient production of biosurfactants: (1) utilization of abundant, inexpensive, and waste biomass as substrate for the production media resulting in low initial raw material costs required for the process and (2) development and optimization of bioprocesses for maximizing biosurfactant production and recovery, leading to reduced operating costs (Saharan et al. 2011; Peirera et al. 2016). Therefore, it appears to be economically viable to produce biosurfactants using economical, renewable resources, such as agricultural wastes, fruit processing industries waste, molasses, vegetable oils, distillery waste, and dairy wastes as substrates (Makkar and Cameotra 2002; Krieger et al. 2010).

3.9 Application of Surfactants in Bioprocessing

Disruption of Cell Biomass In order to address current burning issues of energy security, food-versus-fuel debate and environmental-related issues due to the use of liquid fossil fuels, renewable biofuels are drawing a considerable attention worldwide as substitutes to petroleum-based transportation fuels (Lee 2011). Among various types of renewable fuels, microalgal biodiesel known as "third-generation biofuels" has been considered as one of the best alternatives because of the high photosynthetic efficiency, high growth rate, and high levels of extracted oil (Ahmad et al. 2011). Algal strains, like *Scenedesmus*, *Chlorella*, *Nannochloropsis*, and *Chlamydomonas*, are known to possess a large amount of high-density lipid inclusions (30–60% lipids as dry weight) which can serve as good feedstock for biofuel production (Xin et al. 2011; Bondioli et al. 2012; Seo et al. 2016). However, extraction of lipids from algal cells requires efficient cell disruption methods to allow penetration of solvents into the intracellular inclusions. Different approaches have been developed for microalgal biomass harvesting and cell disruption including

Table 3.4 Major types of biosurfactants produced by different microbial groups

Biosurfactant			
Group	Class	Microorganism	References
Glycolipids	Rhamnolipids	*Pseudomonas aeruginosa* spp. *Ustilago maydis*, *Serratia rubidaea*	Maier and Chavez (2000), Sifour et al. (2007), Teichmann et al. (2007) and Jadhav et al. (2011)
	Trehalolipids	*Mycobacterium* spp. *(tuberculosis*, *bovis*, *smegmatis*, *kansasii*, *malmoense*, *phlei)*, *Rhodococcus (erythropolis*, *opacus*, *ruber)*, *Arthrobacter paraffineus*, *Nocardia* spp., *Corynebacterium* spp. (*fasciens*, *pseudodiphtheria*, *matruchotii*), *Brevibacterium vitarumen*	Franzetti et al. (2010) and Kugler et al. (2015)
	Sophorolipids	*Torulopsis bombicola*, *Torulopsis petrophilum*, *Torulopsis apicola*, *Candida bombicola*, *C. antarctica*, *C. apicola*, *C. stellata*, *C. botisae*	Baviere et al. (1994) and Fesle et al. (2007)
Fatty acids, phospholipids, and neutral lipids	Corynomycolic acid	*Corynebacterium lepus*, *Clavibacter michiganensis*	Gerson and Zajic (1978) and Herman and Maier (2002)
	Spiculisporic acid	*Penicillium spiculisporum*	Ishigami et al. (2000)
	Phosphatidylethanolamine	*Acinetobacter* sp., *Rhodococcus erythropolis*	Appanna et al. (1995) and Santos et al. (2016)
Lipopeptides	Surfactin/iturin	*Bacillus subtilis*, *B. amyloliquefaciens*	Arguelles et al. (2009) and Liu et al. (2015)
	Lichenysin	*Bacillus licheniformis*, *Bacillus subtilis*	Yakimov et al. (1997) and Santos et al. (2016)
Polymeric biosurfactants	Emulsan	*Acinetobacter calcoaceticus* RAG-1	Zosim et al. (1982) and Santos et al. (2016)
	Alasan	*Acinetobacter radioresistens* KA-53	Toren et al. (2001) and Santos et al. (2016)
	Biodispersan	*Acinetobacter calcoaceticus* A2	Rosenberg et al. (1988) and Santos et al. (2016)
	Liposan	*Candida lipolytica*, *C. tropicalis*	Cirigliano and Carman (1984) and Santos et al. (2016)
	Mannoprotein	*Saccharomyces cerevisiae*	Cameron et al. (1988) and Santos et al. (2016)

centrifugation, flocculation, filtration, and flotation for harvesting and microwave heating, ultrasonic cavitation, bead milling, enzymatic, pulsed electric fields, and osmotic shock for cell disruption which are either energy or chemical extensive (Sheng et al. 2011; Liang et al. 2012; Halim et al. 2012).

Because of their proven ability to disrupt membranes, surfactants can play a crucial role in harvesting and disruption of microalgal cells in a cost-effective and energy-efficient manner. The hydrophobic components of surfactants have potential to insert themselves into outer membranes, thereby facilitating the lysis of the cells (Nasirpour et al. 2014). Existing literature suggests that the cationic surfactants could easily bind with a negatively charged microalgal membranes, resulting in effective cell disruption (Huang and Kim 2013; Lai et al. 2016; Salam et al. 2016). A recent study by Seo et al. (2016) described utilization of cationic surfactant-decorated Fe_3O_4 nanoparticles (CS-OTES-MNP) in microalgal cell harvesting, detachment, and cell disruption, schematic illustration of which is presented in Fig. 3.5. Despite the huge potential of surfactant-assisted lipid extraction, there are also certain limitations associated with it. The extent of surfactant binding does not just count on the charge but can also be associated with the hydrophilic-lipophilic interactions between microalgae and surfactant leading to the final cell disruption (Ulloa et al. 2012). Microalgal cell membrane composition not only varies with species but also with the physiological state of a single strain (Gerken et al. 2013; Lai et al. 2016). Thus, any deviation in the cell wall structure can impact the efficiency of surfactant-aided cell disruption method. Therefore, it is imperative to understand correlation between microbial growth cycle and surfactant-aided disruption process.

3.10 Hydrocarbon Bioremediation

Hydrocarbons are the hydrophobic organic chemicals which show restricted water solubility and are toxic and of persistent nature and have an adverse effect on the living forms. Moreover, excessive use of hydrocarbons nowadays has created numerous environmental contamination problems. Additionally, moderate to poor recovery of hydrocarbon contaminants by physicochemical treatments and limited accessibility to microbes and to oxidative and reductive chemicals during the in situ and/or ex situ applications make their removal difficult (Plociniczak et al. 2011). Therefore, biosurfactants hold a great potential in the biological remediation technologies.

Biosurfactant-aided hydrocarbon bioremediation is enhanced due to increase in substrate availability to microorganisms which involves enhancement of the hydrophobicity of the cell surface due to its interactions with the biosurfactant, leading to more effective and easy associations with the microbial cells (Mulligan and Gibbs 2004). Biosurfactants, therefore, consequently can help in enhancing biodegradation and removal of hydrocarbons by the bacteria capable of growing on hydrocarbon contaminants present in polluted soil (Urum and Pekdemir 2004; Nievas et al.

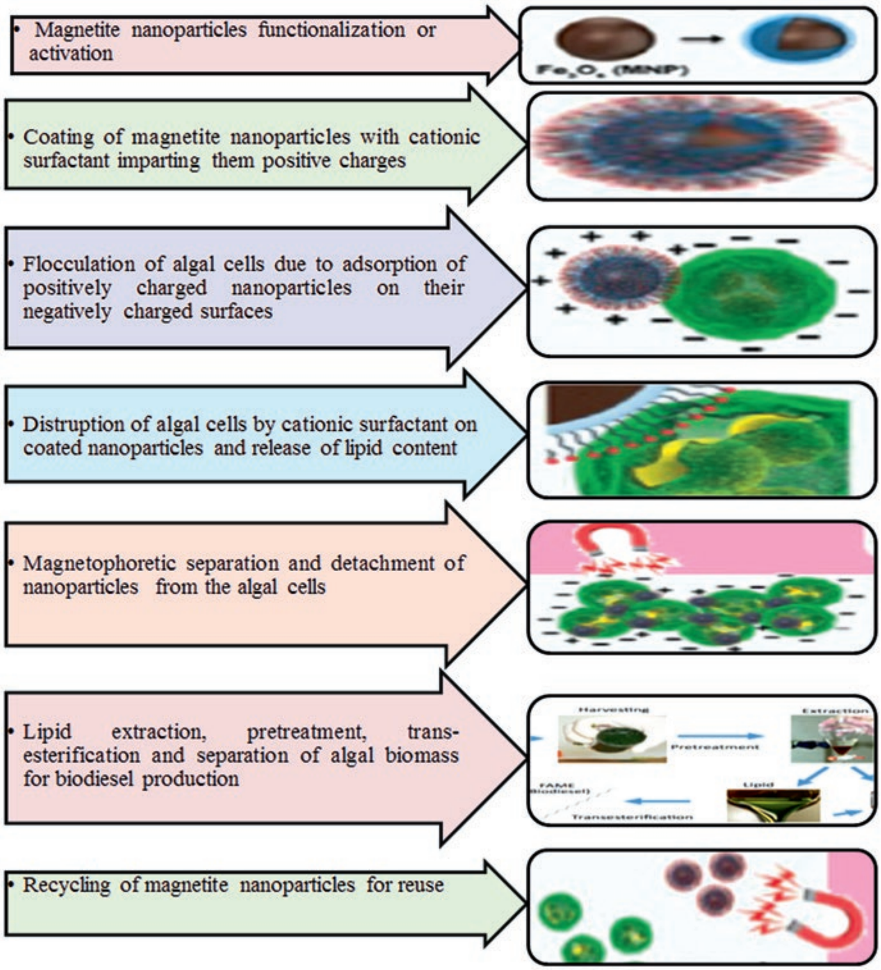


Fig. 3.5 Steps in the utilization of cationic surfactant-decorated magnetite nanoparticles (MNP) in microalgae harvesting, detachment, and cell disruption

2008; Chaprao et al. 2015; Liu et al. 2015; Adrion et al. 2016a; Adrion et al. 2016b; de la Cueva et al. 2016; Sawadogo et al. 2016).

One of the most important applications of biosurfactants is the "microbial enhanced oil recovery" (MEOR) which is generally implied to the recovery of a notable fraction of the residual oil remaining in reservoirs that otherwise is difficult to obtain even after exhausting all the physicomechanical recovery procedures (Banat et al. 2000; Sen 2008). In this process, microbes or their primary or secondary metabolites, such as biosurfactants, biopolymers, acids, solvents, and enzymes, are applied to enhance oil recovery from depleted reservoirs, where biosurfactants stick tightly to the oil/water interface and decrease interfacial tension between oil/

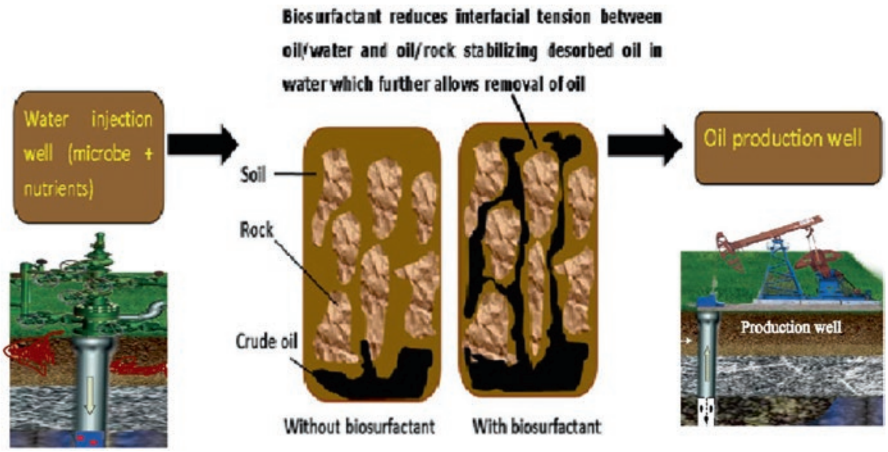


Fig. 3.6 Illustration of role of biosurfactants in microbial enhanced oil recovery (MEOR)

water and oil/rock, leading to the formation of an emulsion which stabilizes the desorbed oil in water. This further aids in the oil removal along with the injection water while decreasing the capillary forces that prevent residual oil from escaping through rock pores (Suthar et al. 2008) as illustrated in Fig. 3.6. MEOR methods can be classified into two main groups: (a) ex situ production of the MEOR metabolites wherein microorganisms are grown using industrial fermenters or mobile plants and then injected into the oil formation as aqueous solutions and (b) in situ production of the MEOR metabolites in which the formation of microbial metabolites takes place directly in the reservoir (Yernazarova et al. 2016). Recently, many authors have also reported applications of biosurfactants in MEOR (Amin 2010; El-Sheshtawy et al. 2015; Golabi 2016).

3.11 Heavy Metal Bioremediation

Due to toxic nature of heavy metals, their contamination in soil ecosystems has serious consequences as even low concentration of heavy metals is very hazardous to the living organisms (Plociniczak et al. 2011). Anionic biosurfactants form complexes with metal with the help of ionic bonds, stronger than the existing metal-soil bonds, and due to the reduced interfacial tension, metal-biosurfactant complexes are detached from the soil surfaces to the soil solution. The cationic biosurfactants replace the same charged metal ions with the help of ion exchange competing for negatively charged surfaces (Mulligan and Gibbs 2004; Juwarkar et al. 2007; Asci et al. 2008). In addition to this, metal ions can also be separated from the soil matrices by the biosurfactant micellar inclusions, wherein the polar head groups of micelles chelate metals, mobilizing them in water as shown in Fig. 3.7 (Mulligan 2005). Many authors have previously reported the utility of biosurfactants in

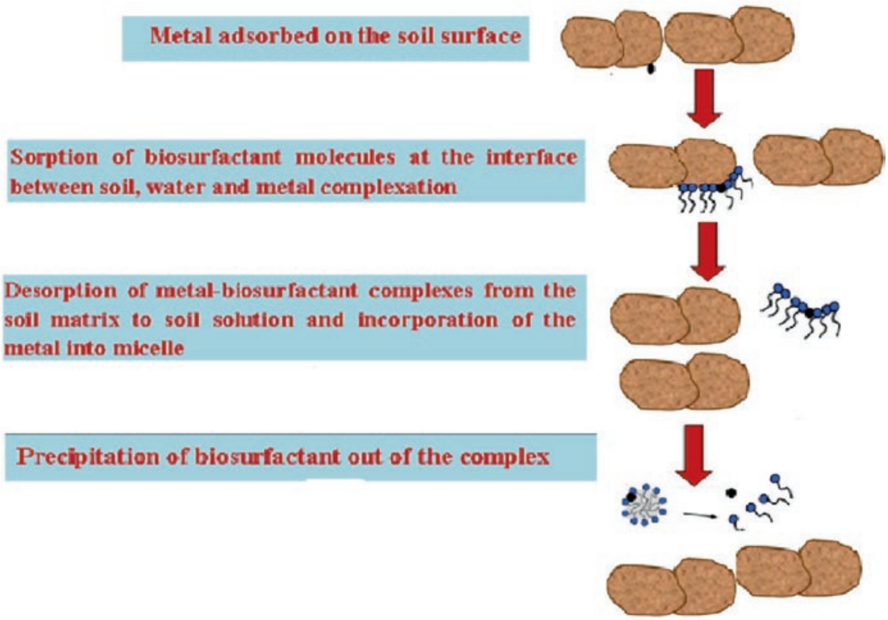


Fig. 3.7 Schematic presentation of biosurfactant-aided heavy metal removal from the soil

bioremediation of soils contaminated with heavy metals (Singh and Cameotra 2004; Juwarkar et al. 2008; Das et al. 2009; Peng et al. 2009; Fu and Wang 2011).

3.12 Bioconversion of Lignocellulosic Biomass

Enormous amount of lignocellulosic biomass in nature has the potential for bioconversion into a variety of high value-added products like biofuels, fine chemicals, and cheap energy sources (Anwar and Gulfraz 2014; Kumar et al. 2016). Lignocellulosic biomass mainly comprises cellulose (30–60%), hemicellulose (20–40%), and lignin (10–25%) which are interconnected in a hetero-matrix constituting roughly 90% of the dry matter, while the rest is composed of ash and other extractives (Rosta Estela and Luis 2013; Nanda et al. 2014). Cellulose and hemicellulose that account for more than 50% of total mass can be potentially converted to sugars for their subsequent conversion to ethanol through a series of processes (Oberoi et al. 2010). Enzymatic hydrolysis and fermentation processes have been combined into several process configurations, such as separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), simultaneous saccharification and co-fermentation (SSCF), and consolidated bioprocessing (CBP) that includes enzyme production, enzymatic saccharification, and fermentation in a single step (Kumar et al. 2016).

Lignocellulosic biomass-derived ethanol is often termed as "second generation" or "2G" offering several advantages, such as greenhouse gas mitigation, near carbon neutrality, lesser dependence on fossil fuels, and improvement in nation's energy security (Naik et al. 2010). The US Department of Energy (DOE) report of 2011 suggests that in the USA alone, more than a billion ton of lignocellulosic biomass is potentially available at ~$60/ton for conversion into > 20 billion gallons of cellulosic biofuels (Perlack and Stokes 2011). Previous reports suggest that the total crop residue available is more than one billion ton in the USA alone and more than nine billion ton worldwide (Lal 2005). Several authors have reported the bioethanol potential of various abundant major agro-wastes generated globally (Kim and Dale 2004; Perlack et al. 2005; Naik et al. 2010; Sarkar et al. 2012).

An immense amount of food waste, such as raw, cooked, edible, and nonedible portions of food crops, is generated during their production, storage, distribution, transportation, processing, and consumption of food stuffs from the household, commercial, and industrial sources. A recent study on global food loss and waste reported a food loss in the range of 27–32% for all the food produced in the world. According to a recent survey in the world, cereal losses at 19–32%, root and tuber losses at 33–60%, and fruit and vegetable losses at 37–55% have been estimated (Global Food Policy Report 2016). Reduction in the food loss and waste can lead to increased global food availability. This waste is a rich source of important biomolecules such as lipids, carbohydrates, amino acids, and phosphates which can be utilized as a substrate for the development of cost-effective biofuels (Pleissner et al. 2013). Carbohydrate-rich food hydrolysate produced after enzymatic hydrolysis of food waste can be transformed into bioethanol, whereas the lipid fraction from hydrolysate can be converted to biodiesel as shown in Fig. 3.8 (Karmee and Lin 2014). Across the globe, a lot of work has been carried out on the tremendous potential of food waste for the generation of biofuels, by different research groups (Kim et al. 2011; Yan et al. 2011; Yan et al. 2013; Yang et al. 2014; Matsakas et al. 2014; Pleissner et al. 2014).

Commercial production of biofuels from lignocellulosic biomass is still hindered by many factors such as (1) biomass recalcitrance requiring effective pretreatment process, (2) high enzyme concentrations to achieve high rate of cellulose hydrolysis, and (3) enzyme adsorption to the lignocellulosic material making enzyme recycling difficult (Gregg and Saddler 1996). The possible ways of inhibition of cellulases by lignin during hydrolysis include (1) nonproductive adsorption of cellulase onto lignin, (2) physical blockage of cellulase on lignocellulose chain structure, and (3) enzyme inhibition due to soluble lignin-derived compounds like ferulic acid, syringaldehyde, vanillin, etc. (Saini et al. 2016). Thus, nonproductive binding of cellulases with lignin results in decreased efficiency of lignocellulosic hydrolysis. Therefore, development of economically feasible cellulose hydrolysis process for ethanol production along with identification of methods to increase enzyme effectiveness is mandated.

Addition of surfactants, such as nonionic detergents and protein, has been reported to significantly increase the enzymatic conversion of cellulose into soluble sugars (Kaar and Holtzapple 1998; Erikssson et al. 2002; Kristensen et al. 2007;

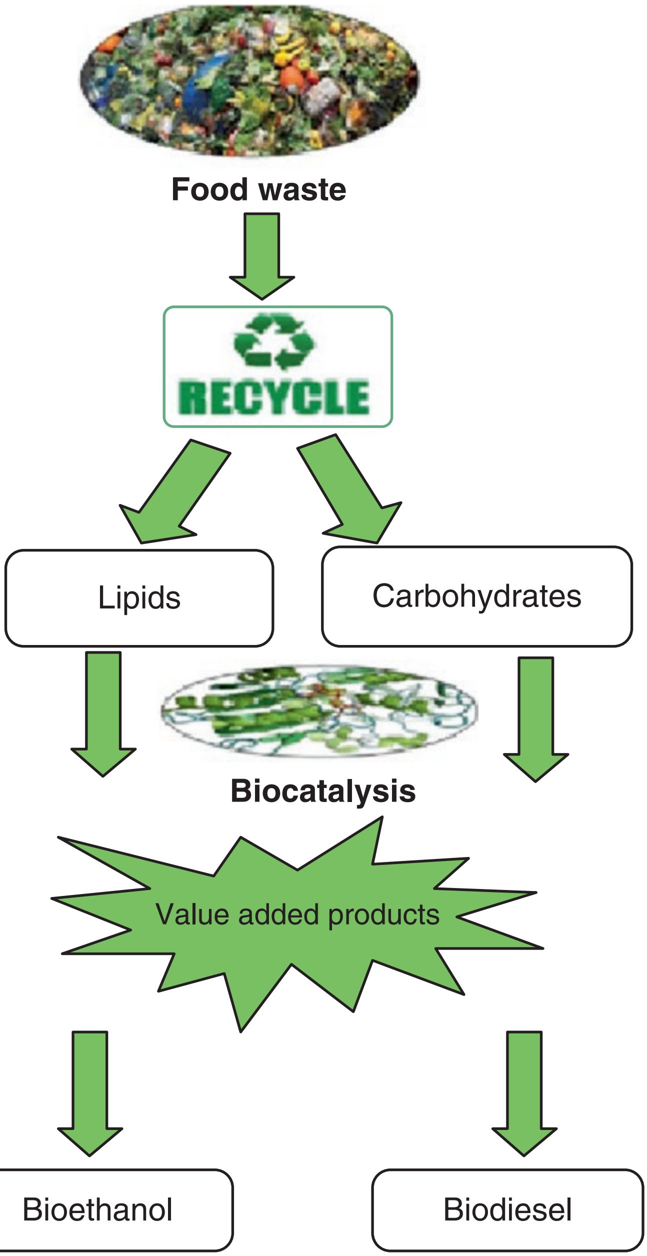


Fig. 3.8 Recycling of food waste into value-added products such as biofuels

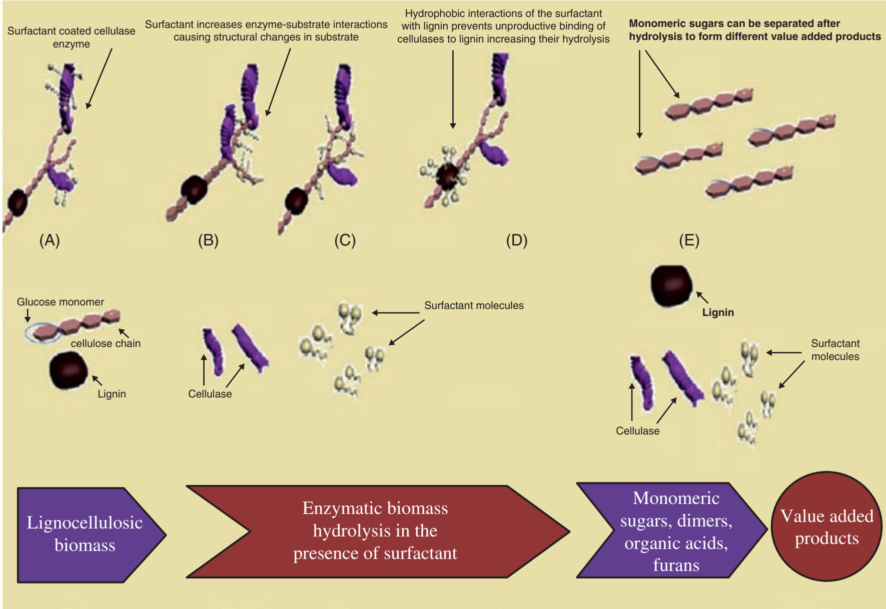


Fig. 3.9 Possible theories explaining enhanced cellulose hydrolysis in the presence of surfactant: (**a**) surfactant "protects" cellulase and increases its stability, (**b**) and (**c**) surfactant increases enzyme-substrate interactions and also causes structural changes in substrate making it more accessible for effective cellulose conversion, (**d**) hydrophobic part of the surfactant binds through hydrophobic interactions to lignin and prevents unproductive binding of cellulases to lignin increasing their efficiency, and (**e**) conversion of cellulose into monomeric units which can be further used for development of value-added products

Bardant et al. 2013; Hseih et al. 2015; Min et al. 2015; Li et al. 2016). On the basis of earlier studies, possible different explanations of surfactant effect on cellulose hydrolysis have been illustrated in Fig. 3.9.

The exact mechanism explaining how surfactants improve enzymatic hydrolysis is still unknown, but several possible explanations have been proposed to describe enhanced surfactant-aided enzymatic hydrolysis of lignocellulosic biomass, and these are:

1. Surfactants enhance removal of lignin by forming emulsions, thereby increasing the access of substrate's reaction sites to the cellulases.
2. Surfactants decrease irreversible, nonproductive adsorption of cellulase to non-productive sites of biomass allowing its availability in solution to have higher activity, thus resulting in higher yields and better recycling of enzymes (Karr and Holtzapple 1998; Park et al. 1992; Eriksson et al. 2002).
3. Enhanced enzyme activity due to improved electrostatic interaction between surfactant and enzyme occurs either by activation of a certain amino acid in the

enzyme active site or by reforming enzyme secondary structure, especially the α-helixes (Eckard et al. 2013a).

4. Surfactants provide protection to enzymes from thermal deactivation and denaturation by reducing the surface tension and viscosity of hydrolysate even after extended incubation period (Yoon and Robyt 2005; Kim et al. 2006; Eckard et al. 2013b). Addition of proteins such as bovine serum albumin (BSA) has also been reported to prevent unproductive binding of cellulases to lignin after blocking its reactive sites (Wang et al. 2013).

Currently, various authors have reported the positive effect of surfactant addition on the enzymatic hydrolysis of lignocellulosics (Qing et al. 2010; Sipos et al. 2011; Parnthong and Kungsanant 2014; Hseih et al. 2015; Min et al. 2015; Li et al. 2016; Mesquita et al. 2016). Liang et al. (2016) measured the effect of molecular structure of lignosulfonate-based polyoxyethylene ether (LS-PEG) on the enzymatic hydrolysis of Avicel and corn stover. They showed that the glucose yield of corn stover increased from 16.7 to 51.9% with a respective increase in PEG content and molecular weight of LS-PEG during hydrolysis. In an unpublished study, we had observed that the addition of 0.2% Tween 20 increased the sugar yield by about 15–20% during hydrolysis of alkali-pretreated sweet sorghum bagasse with crude enzymes produced by *Aspergillus terreus* using optimized parameters, as compared to control, where no surfactant was used. In addition to the sugar concentration, higher productivity of sugars was observed as surfactant-aided hydrolysis was carried out at 60 °C, instead of 50 °C, generally used for industrial applications. Previous studies on enzymatic hydrolysis of pretreated lignocellulosic biomass have reported the use of thermostable crude cellulases and hemicellulases, which helped in achieving a higher sugar yield and productivity (Soni et al. 2010; Srivastava et al. 2014; Rawat et al. 2014; Sharma et al. 2015). It is a well-established fact that the rate of reaction increases with increase in temperature. Therefore, maintaining a temperature of 70–80 °C during hydrolysis with the use of thermostable enzymes and surfactants is likely to improve the sugar productivity manyfold, highly desired by the biofuel industry.

3.13 Future Perspectives

Surfactants represent a major class of industrial chemicals widely used in different industries. Petroleum-derived commercially available chemical surfactants have diverse industrial applications, such as applications in pharmaceuticals, including their role as enhancers for percutaneous absorption, in respiration distress therapy, in suspension aerosols, as emulsifying agents, and in influencing drug absorption (Mishra et al. 2009), in biological systems (Ikegami et al. 2000), in synthesis of nanostructured or mesostructured materials with diverse uses, in health and personal care products (Mainkar and Jolly 2001), in food industries (Kralova and Sjöblom 2009), and also in crop protection (Green and Beestman 2007). Notwithstanding these advantages, the toxicity and persistence of surfactants in different environmental situations have also been highlighted by several authors (Ying 2006; Ivankovic and Hrenovic 2010). Thus, there is an imminent requirement to realize the effects of surfactants during their normal applications as well as accidental spills in the environment.

Biosurfactants due to their diverse, less toxic, and biodegradable nature have gained importance in recent times as viable alternatives to the chemical surfactants. There is a wide range of potential commercial applications of biosurfactants in diverse industries, such as pulp and paper industry, food industry, textiles, pharmaceutical industry as therapeutic agents, paint industry, remediation processes, cell-biomass disruption, bioprocessing, and even uranium ore processing (Banat et al. 2010; Silva et al. 2014; Peireira et al. 2016). One of the emerging areas of research using biosurfactants is the conversion of agricultural biomass into sugars for their subsequent conversion to liquid fuels. There is very scanty information available on biosurfactant-aided enzymatic hydrolysis of pretreated biomass. The use of biosurfactants during pretreatment might not only yield good results for lignin deconstruction/removal but may also reduce the higher energy required to achieve the same level of efficiency. This coupled with high-temperature biosurfactant-aided enzymatic hydrolysis as discussed elsewhere is likely to revolutionize the research in second-generation bioethanol production. It is well recognized that pretreatment and hydrolysis are the most cost- and energy-intensive operations in conversion of lignocellulosic biomass to liquid fuels (Parnthong and Kungsanant 2014; Mesquita et al. 2016).

Similarly, the use of biosurfactants in developing valuable compounds from fruit and vegetable processing waste holds promise for the future. Since the fruit and vegetable processing waste is high in moisture, biosurfactants in combination with enzymes or other extraction methods may help in efficient extraction of pigments, carotenoids, and other nutritionally important compounds for their use in the development of functional foods. Because of the presence of lower lignin and high carbohydrates, fruit and vegetable processing wastes offer good opportunities for production of bioethanol and other value-added products. Use of surfactants/biosurfactants in improving ethanol productivity from the fruit and vegetable processing residues is likely to draw attention of many researchers involved in biofuel research.

Commercial production and development of biosurfactants is dictated by their safety issues and high production cost. Biosurfactants, currently under investigation, such as sophorolipids and rhamnolipids have not been reported to pose any safety or health issue (Marchant and Banat 2012). However, in certain isolated cases, rhamnolipids can act as immune modulators or as virulence factors in *P. aeruginosa* infections known as an opportunistic pathogen (McClure and Schiller 1996; Zulianello et al. 2006). Commercial production of rhamnolipid has been initiated by a company, Jeneil Biotech, Milwaukee, USA (www.jenielbiotech.com), which has reported no health issues associated with its use. Furthermore, large-scale production of sophorolipids, generally produced by yeasts, is also already underway in Asia with no reported health/safety issues (Marchant and Banat 2012).

One of the ways to reduce the overall costs is through improving the stability of biosurfactants. Another way to reduce the high production costs is to use a wide variety of microorganisms, such as *Bacillus*, *Candida*, *Pseudomonas*, *Thiobacillus*, etc., for producing biosurfactants using various renewable substrates, such as sugars, oils, alkanes, and agro-industrial wastes including molasses, potato processing wastes, olive oil mill effluent, plant oil extracts and waste, distillery and whey wastes, by-products of vegetable industries, dairy and sugar industry wastes, and cassava wastewater (Makkar and Cameotra 1999; Youssef et al. 2004; Makkar et al. 2011). However, these microbes cannot be used for commercial production of biosurfactants on a large scale due to their low productivity. Thus, the microbial strain producing biosurfactants should be carefully selected and engineered for enhanced productivity. Moreover, the production process should also be engineered in such a way so as to minimize overall capital, operating, maintenance, and product recovery costs (Reis et al. 2013).

Keeping in mind the demand and need for green technology, biosurfactants can also have a potential application in the synthesis of nanoparticles, which is an emerging promising environment-compatible method. Use of biosurfactants reduces the formation of aggregates facilitating homogeneous and uniform morphology of the nanoparticles during synthesis (Kiran et al. 2010; Mujumdar et al. 2016). Nano-emulsions are advantageous because of the Brownian motion of very small droplets causing a significant deduction in the gravity force. This further inhibits their coalescence, since these droplets are non-deformable, and hence, surface fluctuations are avoided. Consequently, low surface tension of the whole system results in high penetration of active and the small-sized droplets allowing their enhanced uniform rapid deposition on substrates (Morsy 2014). Reddy et al. (2009) reported stabilization of silver nanoparticles for 2 months using surfactin, known as a biodegradable, less toxic stabilizing agent. These surfactant-aided nano-emulsions have diverse applications in agrochemicals, as lubricants and cutting oils and corrosion inhibitors, in remediation technology, in pharmaceutics, in cosmetics, in foods, and in personal care products (Oliveira et al. 2014; Morsy 2014; Jaiswal et al. 2015; Mujumdar et al. 2016; Santos et al. 2016). Therefore, there is an imperative need to focus research efforts on the biosurfactant-mediated stabilization of the nanoparticles for diverse industrial applications.

3.14 Conclusions

- Biosurfactants are potential replacements for synthetic surfactants in several industrial processes due to their biodegradability and lower toxicity.
- Presently, despite of their many advantages, high production costs and shortage of detailed information on toxicity testing of biosurfactants make them economically incompetent in comparison to chemically produced surfactants available in the market.
- Measures selected to target simplification and optimization of the kinds of the products for specific applications, such as use of sterilized or pasteurized fermentation broth without the requirement for extraction, concentration, or purifi-

cation of the biosurfactant, may remarkably decrease the process production cost.

- Optimization of upstream and downstream approaches during the production processes may also have a significant influence on the overall cost reduction. Success of biosurfactants in bioremediation will be in need of specific targeting and complete information of the physicochemical nature of the pollutant-affected areas.
- Role of biosurfactants in MEOR has numerous utilities with respect to environment, but extensive research is still required for ex situ production and commercial application.
- With increased efforts on the development of improved and cost-efficient application technologies, genetic engineering, and strain improvement techniques and production processes, biosurfactants are predicted to be one of the most multifaceted and valued compounds for use in various processes in the coming time.

References

Abraham M (2003) Wetting of hydrophobic rough surfaces: to be heterogeneous or not to be. Langmuir 4:8343–8348

Adrion AC, Nakamura J, Shea D, Aitken MD (2016a) Screening nonionic surfactants for enhanced biodegradation of polycyclic aromatic hydrocarbons remaining in oil after conventional biological treatment. Environ Sci Technol 50(7):3838–3845. doi:10.1021/acs.est.5b05243

Adrion AC, Singleton DR, Jun N, Damian S, Aitken MD (2016b) Improving polycyclic aromatic hydrocarbon biodegradation in contaminated soil through low-level surfactant addition after conventional bioremediation. Environ Eng Sci 33(9):659–670. doi:10.1089/ees.2016.0128

Ahmad AL, Yasin NHM, Derek CJC, Lim JK (2011) Microalgae as a sustainable energy source for biodiesel production: a review. Sust Energ Rev 15:584–593

Al-Bhary SN, Al-Wahaibi YM, Elshafie AE, Al-Bemani AS, Joshi SJ, Al-akhmari HS, Al-Sulaimani HS (2013) Biosurfactant production by *Bacillus subtilis* B20 using date molasses and its possible application in enhanced oil recovery. Int Biodeterior Biodegrad 81:141–146

Alvira P, Ballesteros M, Negro MJ (2013) Progress on enzymatic saccharification technologies for biofuels production. In: Gupta VK, Tuohy MG (eds) Biofuel technologies: recent developments. Springer, Berlin, Germany, pp 145–169

Amin GA (2010) A potent biosurfactant producing bacterial strain for application in enhanced oil recovery applications. J Pet Environ Biotechnol 1:104–111. doi:10.4172/2157-7463.1000104

Anwar Z, Gulfraz IM (2014) Agro-industrial lignocellulosic biomass a key to unlock the future bio-energy: a brief review. J Radiation Res Appl Sci 7:163–173

Appanna VD, Finn H, Pierre M (1995) Exocellular phosphatidylethanolamine production and multiple-metal tolerance in *Pseudomonas fluorescens*. FEMS Microbiol Lett 131:53–56

Arguelles-Arias A, Ongena M, Halimi B (2009) *Bacillus amyloliquefaciens* GA1 as a source of potent antibiotics and other secondary metabolites for biocontrol of plant pathogens. Microb Cell Factories 8:63–71

Arparna A, Srinikethan G, Hedge S (2011) Effect of addition of biosurfactant produced by *Pseudomonas* ssp. on biodegradation of crude oil. In: 2nd International proceedings of chemical, biological and environmental engineering, Singapore, 26–28 February 2011, vol 6, p 71–75

Asci Y, Nurbaş M, Acikel YS (2008) A comparative study for the sorption of Cd(II) by soils with different clay contents and mineralogy and the recovery of Cd(II) using rhamnolipid biosurfactant. J Hazd Mater 154:663–673

Aulwar U, Awasthi RS (2016) Production of biosurfactant and their role in bioremediation. J Ecosys Ecograph 6:202. doi:10.4172/2157-7625.1000202
Azarmi R, Ashjaran A (2015) Type and application of some common surfactants. J Chem Pharm Res 7(2):632–640
Balan V (2014) Current challenges in commercially producing biofuels from lignocellulosic biomass. Hindawi Publishing Corporation ISRN Biotechnology 463074. doi:10.1155/2014/463074
Banat IM, Makkar RS, Cameotra SS (2000) Potential commercial applications of microbial surfactants. Appl Environ Microbiol 53:495–508
Banat IM, Franzetti A, Gandolfi I, Bestetti G, Martinotti MG, Fracchia L, Smyth TJ, Marchant R (2010) Microbial biosurfactants production, applications. Appl Microbiol Biotechnol 87:427–444
Banat IM, Satpute SK, Cameotra SS (2014) Cost effective technologies and renewable substrates for biosurfactants production. Front Microbiol 5:1–18
Bardant TB, Abimanyu SH, Hanum AK (2013) Effect of non-ionic surfactant addition to cellulase performance in high substrate loading hydrolysis of palm oil EFB and water hyacinth. Indo J Chem 13(1):53–58
Baviere M, Degouy D, Lecourtier J (1994) Process for washing solid particles comprising a sophoroside solution. US Patent 5:32–407
Bondioli P, Bella LD, Rivolta G, Zittelli GC, Bassi N, Rodolfi L, Casini D, Prussi M, Chiaramonti D, Tredici MR (2012) Oil production by the marine microalgae *Nannochloropsis* sp. F and M-M24 and *Tetraselmis suecica* F and M-M33. Bioresour Technol 114:567–572
BP Statistical Review of World Energy (2016) Centre for Energy Economics Research and Policy, Heriot-watt university, 65th edn. Whitehouse Associates/Pureprint Group Limited, London, pp 1–48
Cameron DR, Cooper DG, Neufeld RJ (1988) The mannoprotein of *Saccharomyces cerevisiae* is an effective bioemulsifier. Appl Environ Microbiol 54:1420–1425
Campos JM, Stamford TLM, Sarubbo LA, Luna JM, Rufino RD, Banat IM (2013) Microbial biosurfactants as additives for food industries. Biotechnol Prog 29:1097–1108
Carriquiry MA, Du X, Timilsina GR (2011) Second generation biofuels: economics and policies. Energ Pol 39(7):4222–4234
Carter KC, Puig-Sellart M (2016) Nanocarriers made from non-ionic surfactants or natural polymers for pulmonary drug delivery. Curr Pharm Des 22(22):3324–3331
Chaprao MJ, Ferreira INS, Correa PF, Rufino RD, Luna JM, Silva EJ, Sarubbo LA (2015) Application of bacterial and yeast biosurfactants for enhanced removal and biodegradation of motor oil from contaminated sand. Electron J Biotechnol 18:471–479
Chavez SG, Maier RM (2011) Biosurfactants: a general overview. In: Chavez SG (ed) Biosurfactants. Springer-Verlag, Berlin, pp 1–11
Christofi N, Ivshina IB (2002) Microbial surfactants and their use in field studies of soil remediation. J Appl Microbiol 93:915–929
Cirigliano MC, Carman GM (1984) Purification and characterization of liposan, a bioemulsifier from *Candida lipolytica*. Appl Environ Microbiol 50:846–850
Das P, Mukherjee S, Sen R (2009) Biosurfactant of marine origin exhibiting heavy metal remediation properties. Bioresour Technol 100:4887–4890
Desai JD, Banat IM (1997) Microbial production of surfactants and their commercial potential. Microbiol Mol Biol Res 61:47–64
de la Cueva SC, Rodríguez CH, Cruz NOS (2016) Changes in bacterial populations during bioremediation of soil contaminated with petroleum hydrocarbons. Water Air Soil Pollut 227:91. doi:10.1007/s11270-016-2789-z
Eckard AD, Muthukumarappan K, Gibbons W (2013a) A review of the role of amphiphiles in biomass to ethanol conversion. Appl Sci 3:396–419. doi:10.3390/app3020396
Eckard AD, Muthukumarappan K, Gibbons W (2013b) Enzyme recycling in a simultaneous and separate saccharification and fermentation of corn stover: comparing polymeric micelles of surfactants and polypeptides. Bioresour Technol 132:202–209

El-Sheshtawy HS, Aiada I, Osmanb ME, Abo-Elnasr AA, Kobisya AS (2015) Production of biosurfactant from *Bacillus licheniformis* for microbial enhanced oil recovery and inhibition the growth of sulfate reducing bacteria. Egypt J Petr 24(2):155–162

Eriksson T, Borjesson J, Tjerneld F (2002) Mechanism of surfactant effect in enzymatic hydrolysis of lignocellulose. Enzym Microb Technol 31:353–364

Felse PA, Shah V, Chan J (2007) Sophorolipid biosynthesis by *Candida bombicola* from industrial fatty acid residues. Enz Microbiol Technol 40:316–323

Franzetti A, Gandolfi I, Bestetti G, Smyth TJ, Banat IM (2010) Production and applications of trehalose lipid biosurfactants. Eur J Lipid Sci Tech 112:617–627

Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: a review. J Env Manag 92(3):407–418

GAF (1950) General Aniline and Film Corp. for their surface active products. For an example of one of GAF Corp's. early advertisements promoting their trademarked surfactants. Business Week, March 11, p 42

Gerken HG, Donohoe B, Knoshaug EP (2013) Enzymatic cell wall degradation of *Chlorella* vulgaris and other microalgae for biofuels production. Planta 237:239–253. doi:10.1007/s00425-012-1765-0

Gerson OF, Zajic JE (1978) Surfactant production from hydrocarbons by *Corynebacterium lepus,* sp. nov. and *Pseudomonas asphaltenicus*, sp. nov. dev. Ind J Microbiol 19:577–599

Global Food Policy Report (2016) International Food Policy Research Institute (IFPRI), Washington, DC. ISBN: 978-0-89629-582-7, pp 23–34. doi:10.2499/9780896295827

Golabi E (2016) Experimental study of effect of microbial enhanced oil recovery on rag Sefid reservoir. Int J Chem Stud 4(1):43–45

Green JM, Beestman GB (2007) Recently patented and commercialized formulation and adjuvant technology. Crop Protec 26(3):320–327

Greenwell HC, Loyd-Evans M, Wenner C (2012) Biofuels, science and society. Interface Focus 3:1–4

Gregg D, Saddler JN (1996) Factors affecting cellulose hydrolysis and the potential of enzyme recycle to enhance the efficiency of an integrated wood to ethanol process. Biotechnol Bioeng 51:375–383

Halim R, Danquah MK, Webley PA (2012) Extraction of oil from microalgae for biodiesel production: a review. Biotechnol Adv 30(3):709–732. doi:10.1016/j.biotechadv.2012.01.001

Hall M, Bansal P, Lee JH, Realff MJ, Bommarius AS (2010) Cellulose crystallinity-a key predictor of the enzymatic hydrolysis rate. FEBS J 277(6):1571–1582

Herman DC, Maier RM (2002) Biosynthesis and applications of glycolipid and lipopeptide biosurfactants. In: Kuo TM, Gardner HW (eds) Lipid biotechnology. Marcel Dekker, New York, pp 629–654

Hsieh CC, Cannella D, Jørgensen H, Felby C, Thygesen LG (2015) Cellobiohydrolase and endoglucanase respond differently to surfactants during the hydrolysis of cellulose. Biotechnol Biofuels 8(52):1–10. doi:10.1186/s13068-015-0242-y

Huang WC, Kim JD (2013) Cationic surfactant-based method for simultaneous harvesting and cell disruption of a microalgal biomass. Bioresour Technol 149:579–581

Information Handling Services (2016) Chemical Economics Handbook: Surfactants, household detergents and their raw materials, p 16–19. (www.ihs.com/products/surfactants-household-detergents-chemical-economics-handbook.html)

Ikegami M, Whitsett JA, Jobe A, Ross G, Fisher J, Korfhagen T (2000) Surfactant metabolism in SP-D gene-targeted mice. Am J Physiol Lung Cell Mol Physiol 279(3):468–476

Ishigami Y, Zhang Y, Ji F (2000) Spiculisporic acid. Functional development of biosurfactants. Chim Oggi 18:32–34

Ivankovic T, Hrenovic J (2010) Surfactants in the environment: a review. Arh Hig Rada Toksikol 61:95–110. doi:10.2478/10004-1254-61-2010-1943

Jadhav M, Kalme S, Tamboli D (2011) Rhamnolipid from *Pseudomonas desmolyticum* NCIM-2112 and its role in the degradation of brown 3REL. J Basic Microbiol 51:1–12

Jaiswal M, Dudhe R, Sharma PK (2015) Nanoemulsion: an advanced mode of drug delivery system. 3. Biotech 5(2):123–127. doi:10.1007/s13205-014-0214-0

Jeoh T, Ishizawa CI, Davis MF, Himmel ME, Adney WS, Johnson DK (2007) Cellulase digestibility of pretreated biomass is limited by cellulose accessibility. Biotechnol Bioeng 98(1):112–122

Juwarkar AA, Nair A, Dubey KV, Singh SK, Devotta S (2007) Biosurfactant technology for remediation of cadmium and lead contaminated soils. Chemosphere 68:1996–2002

Juwarkar AA, Dubey KV, Nair A, Singh SK (2008) Bioremediation of multi-metal contaminated soil using biosurfactant—a novel approach. Ind J Microbiol 48:142–146

Kaar WE, Holtzapple M (1998) Benefits from tween during enzymatic hydrolysis of corn stover. Biotechnol Bioeng 59:419–427

Kapadia SG, Yagnik BN (2013) Current trend and potential for microbial biosurfactants. Asian J Exp Biol Sci 4:1–8

Karmee SK, Lin CSK (2014) Valorisation of food waste to biofuel: current trends and technological challenges. Sustainable Chem Proc 2:22–32

Kim S, Dale BE (2004) Global potential bioethanol production from wasted crops and crop residues. Biomass Bioenergy 26:361–375

Kim J, Grate JW, Wang P (2006) Nanostructures for enzyme stabilization. Chem Eng Sci 61(3):1017–1026

Kim JH, Lee JC, Pak D (2011) Feasibility of producing ethanol from food waste. Waste Manag 31:2121–2125

Kiran GS, Sabu A, Selvin J (2010) Synthesis of silver nanoparticles by glycolipid biosurfactant produced from marine *Brevibacterium casei* MSA19. J Biotechnol 148:221–225

Kralova I, Sjoblom J (2009) Surfactants used in food industry: a review. J Dispers Sci Technol 30:1363–1383

Krieger N, Doumit C, David AM (2010) Production of microbial biosurfactants by solid-state cultivation. Adv Exp Med Biol 672:203–210

Kristensen JB, Borjesson J, Maria H, Tjerneld BF, Jorgensen H (2007) Use of surface active additives in enzymatic hydrolysis of wheat straw lignocellulose. Enz Microb Technol 40:888–895

Kugler JH, Le Roes-Hill M, Syldatk C, Hausmann R (2015) Surfactants tailored by the class Actinobacteria. Front Microbiol 6:212–219. doi:10.3389/fmicb.2015.00212

Kumar R, Tabatabaei M, Karimi K, Horváth IS (2016) Recent updates on lignocellulosic biomass derived ethanol – a review. Biofuel Res J 9:347–356

Lai YJS, De Francesco F, Aguinaga A, Parameswaran P, Rittmanna BE (2016) Improving lipid recovery from *Scenedesmus* wet biomass by surfactant-assisted disruption. Green Chem 18:1319–1326

Lal R (2005) World crop residues production and implications of its use as a biofuel. Environ Int 31(4):575–584

Ławniczak L, Marecik R, Chrzanowski L (2013) Contributions of biosurfactants to natural or induced bioremediation. Appl Microbiol Biotechnol 97:2327–2339

Lee DH (2011) Algal biodiesel economy and competition among biofuels. Bioresour Technol 102:43–49

Lee RA, Lavoie JM (2013) From first – to third-generation biofuels: challenges of producing a commodity from a biomass of increasing complexity. Animal Front 3(2):6–11

Li Y, Sun Z, Ge X, Zhang J (2016) Effects of lignin and surfactant on adsorption and hydrolysis of cellulases on cellulose. Biotechnol Biofuels 9(20):1–10. doi:10.1186/s13068-016-0434-0

Liang K, Zhang Q, Cong W (2012) Enzyme-assisted aqueous extraction of lipid from microalgae. J Agric Food Chem 60(47):11771–11776. doi:10.1021/jf302836v

Liang LX, Qing QX, Ming LH, Hao LZ, Xin ZN, Hao HJ, Xia PY (2016) Enhancement of lignosulfonate-based polyoxyethylene ether on enzymatic hydrolysis of lignocelluloses. Indus Crops Prod 80:86–92

Liu JF, Mbadinga SM, Yang SZ, Gu JD, Mu BM (2015) Chemical structure, property and potential applications of biosurfactants produced by *Bacillus subtilis* in petroleum recovery and spill mitigation. Int J Mol Sci 16:4814–4837. doi:10.3390/ijms16034814

Luo L, van der Voet E, Huppes G (2010) Biorefining of lignocellulosic feedstock—technical, economic and environmental considerations. Bioresour Technol 101(13):5023–5032
Maier RM, Chávez SG (2000) *Pseudomonas aeruginosa* rhamnolipids: biosynthesis and potential applications. Appl Microbiol Biotechnol 54:625–633
Mainkar AR, Jolly CI (2001) Formulation of natural shampoos. Int J Cosmetic Sci 23:59–62
Makkar RS, Cameotra SS (1999) Biosurfactant production by microorganisms on unconventional carbon sources. J Surfact Deterg 2:2–16
Makkar RS, Cameotra SS (2002) An update on use of unconventional substrates for biosurfactants production and their new applications. Appl Microbiol Biotechnol 58:428–434
Makkar RS, Banat IM, Cameotra SS (2011) Advances in utilization of renewable substrates for biosurfactant production. AMB Express 1:5–17
Marchant R, Banat IM (2012) Microbial biosurfactants: challenges and opportunities for future exploitation. Trends Biotechnol 30:558–565. doi:10.1016/j.tibtech.2012.07.003
Matsakas L, Kekos D, Loizidou M, Christakopoulos P (2014) Utilization of household food waste for the production of ethanol at high dry material content. Biotechnol Biofuels 7:4–12
McClure CD, Schiller NL (1996) Inhibition of macrophage phagocytosis by *Pseudomonas aeruginosa* rhamnolipids in vitro and in vivo. Curr Microbiol 33:109–117
Menon V, Rao M (2012) Trends in bioconversion of lignocellulose: biofuels, platform chemicals and biorefinery concept. Prog Energ Combustion Sci 38(4):522–550
Mesquita JF, Ferraz A, Aguiar A (2016) Alkaline-sulfite pretreatment and use of surfactants during enzymatic hydrolysis to enhance ethanol production from sugarcane bagasse. Bioprocess Biosyst Eng 39:441–448. doi:10.1007/s00449-015-1527-z
Min BC, Bhayani BV, Jampana V, Ramarao BV (2015) Enhancement of the enzymatic hydrolysis of fines from recycled paper mill waste rejects. Bioresour Bioproc 2(40):1–10. doi:10.1186/s40643-015-0068-2
Mishra M, Muthuprasanna P, Surya prabha K, Rani PS, Babu IAS, Chandiran IS, Arunachalam G, Shalini S (2009) Basics and potential applications of surfactants – a review. Int J PharmTech Research, 1: 1354-1365, ISSN:0974-4304
Morsy SMI (2014) Review article: role of surfactants in nanotechnology and their applications. Int J Curr Microbiol App Sci 3(5):237–260
Mujumdar S, Bashetti S, Pardeshi S, Thombre RS (2016) Industrial applications of biosurfactants. In: Thangadurai D, Sangeetha J (eds) Industrial biotechnology: sustainable production and bioresource utilization. CRC Press, Boca Raton, pp 61–90. ISBN 177188262X, 9781771882620
Mulligan CN (2005) Environmental applications for biosurfactants. Environ Pollut 133:183–198
Mulligan CN, Gibbs BF (2004) Types, production and applications of biosurfactants. Proc Ind Nat Sci Acad 1:31–55
Naik SN, Goud VV, Rout PK, Dalai AK (2010) Production of first and second generation biofuels: a comprehensive review. Renew Sust Energ Rev 14:578–597
Nanda S, Mohammad J, Reddy S, Kozinski J, Dalai A (2014) Pathways of lignocellulosic biomass conversion to renewable fuels. Biomass Conver Bioref 4:157–191. doi:10.1007/s13399-013-0097-z
Naqvi M, Yan J (2015) First-generation biofuels. Handbook of clean energy systems. Wiley, Chichester, pp 1–18. doi:10.1002/9781118991978.hces207
Nasirpour N, Mousavi SM, Shojaosadati SA (2014) A novel surfactant-assisted ionic liquid pretreatment of sugarcane bagasse for enhanced enzymatic hydrolysis. Bioresour Technol 169:33–37
Nievas ML, Commendatore MG, Estevas JL, Bucala V (2008) Biodegradation pattern of hydrocarbons from a fuel oil-type complex residue by an emulsifier-producing microbial consortium. J Hazard Matter 154:96–104
Oberoi HS, Vadlani PV, Madl RL, Saida L, Abeykoon JP (2010) Ethanol production from orange peels: two-stage hydrolysis and fermentation studies using optimized parameters through experimental design. J Agric Food Chem 58:3422–3429
Park JW, Takahata Y, Kajiuchi T, Akehata T (1992) Effects of nonionic surfactant on enzymatic hydrolysis of used newspaper. Biotechnol Bioeng 39:117–120

Parnthong J, Kungsanant S (2014) Statistical optimization for application of nonionic surfactants in enzymatic hydrolysis of palm fiber for ethanol production. Int J Chem Eng App 5:23–25
Peng JF, Song YH, Yuan P, Cui XY, Qiu GL (2009) The remediation of heavy metals contaminated sediment. J Hazard Mat 161(30):633–640
Pereira BL, Francisco SM, da Silva SS (2016) Recent advances in sustainable production and application of biosurfactants in Brazil and Latin America. Indus Biotechnol 12(1):31–39. doi:10.1089/ind.2015.0027
Perlack RD, Wright LL, Turhollow AF, Graham RL, Stokes BJ, Erbach DC (2005) Biomass as a feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply. Oak Ridge National laboratory, US Department of Agriculture (USDA), pp 1–54. Available electronically at: http://www.osti.gov/bridge
Perlack RD, Stokes BJ (2011) US billion-ton update: biomass supply for a bioenergy and bioproducts industry. US Department of Energy, Oak Ridge National Laboratory, Oak Ridge
Pleissner D, Lam WC, Sun Z, Lin CSK (2013) Food waste as nutrient source in heterotrophic microalgae cultivation. Bioresour Technol 137:139–146
Pleissner D, Kwan TH, Lin CSK (2014) Fungal hydrolysis in submerged fermentation for food waste treatment and fermentation feedstock preparation. Bioresour Technol 158:48–54
Płociniczak MP, Płaza GA, Seget ZP, Cameotra SS (2011) Environmental applications of biosurfactants: recent advances. Int J Mol Sci 12:633–654. doi:10.3390/ijms12010633
Pothiraj C, Kanmani P, Balaji P (2006) Bioconversion of lignocellulose materials. Mycobiol 34(4):159–165
Qing Q, Yang B, Wyman CE (2010) Impact of surfactants on pretreatment of corn stover. Bioresour Technol 101:5941–5951
Rahman PKSM, Gakpe E (2008) Production, characterization and applications of biosurfactants-review. Biotechnol 7:360–370. doi:10.3923/biotech.2008.360.370
Rawat R, Srivastava N, Chadha BS, Oberoi HS (2014) Generating fermentable sugars from rice straw using functionally active cellulolytic enzymes from *Aspergillus niger* HO. Energ Fuels 28:5067–5075. doi:10.1021/ef500891g
Reddy AS, Chen CY, Baker SC, Chen CC, Jean JS, Fan CW, Chen HR, Wang JC (2009) Synthesis of silver nanoparticles using surfactin: a biosurfactant stabilizing agent. Mater Lett 63:1227–1230
Reis RS, Pacheco GJ, Pereira AG, Freire DMG (2013) Biosurfactants: production and applications. Chapter 2 in biodegradation-life of science, pp 31–63. http://dx.doi.org/10.5772/56144
Rosa Estela QCE, Luis FMJ (2013) Hydrolysis of biomass mediated by cellulases for the production of sugars. In: Chandel AK, da- Silva SS (eds) Sustainable degradation of lignocellulosic biomass-techniques, applications and commercialization. Rijeka, Croatia, pp 119–155. doi:10.5772/53719
Rosenberg E, Rubinovitz C, Legmann R, Ron EZ (1988) Purification and chemical properties of *Acinetobacter calcoaceticus* A2 Biodispersan. Appl Environ Microbiol 54:323–326
Sachdev DP, Cameotra SS (2013) Biosurfactants in agriculture. Appl Microbiol Biotechnol 97:1005–1016
Saharan BS, Sahu RK, Sharma D (2011) A review on biosurfactants: fermentation, current developments and perspectives. Genetic Eng Biotechnol J 29:1–14
Saini JK, Patel AK, Adsul M, Singhania RR (2016) Cellulase adsorption on lignin: a roadblock for economic hydrolysis of biomass. Renew Energy 98:29–42
Sajjadi S, Jahanzad F, Yianneskis M, Brooks BW (2003) Phase inversion in abnormal O/W/O emulsions: effect of surfactant hydrophilic−lipophilic balance. Ind Eng Chem Res 42(15):3571–3577. doi:10.1021/ie021044e
Salager JL (2002) Surfactants: types and uses. Laboratory of formulation, interfaces rheology and processes, FIRP booklet E300:1–48
Salam KA, Velasquez-Orta SB, Harvey AP (2016) Surfactant-assisted direct biodiesel production from wet *Nannochloropsis oculata* by in situ transesterification/reactive extraction. Biofuel Res J 9:366–371

Samiey B, Cheng CH, Wu J (2014) Effects of surfactants on the rate of chemical reactions. J Chem Article ID 908476:1–14. http://dx.doi.org/10.1155/2014/908476

Santos DKF, Rufino RD, Luna JM, Santos VA, Salgueiro AA, Sarubbo LA (2013) Synthesis and evaluation of biosurfactant produced by *Candida lipolytica* using animal fat and corn steep liquor. J Pet Sci Eng 105:43–50

Santos DKF, Rufino RD, Luna JM, Santos VA, Sarubbo LA (2016) Review: biosurfactants multifunctional biomolecules of the 21st century. Int J Mol Sci 17:401–432. doi:10.3390/ijms17030401

Sarkar N, Ghosh SK, Bannerjee S, Aikat K (2012) Bioethanol production from agricultural wastes: an overview. Renew Energ 37:19–27

Sawadogo A, Otoidobiga HC, Nitiema LW, Traore AS, Dianou D (2016) Optimization of hydrocarbons biodegradation by bacterial strains isolated from wastewaters in Ouagadougou, Burkina Faso: case study of SAE 40/50 used oils and diesel. J Agric Chem Environ 5:1–11. doi.org/10.4236/jacen.2016.51001

Schramm LL, Stasiuk EN, Marangoni GD (2003) Surfactants and their applications. Ann Rep Prog Chem 99:30–48. doi:10.1039/b208499f

Sekhon BS (2013) Surfactants: pharmaceutical and medicinal aspects. J Pharma Technol Res Manage 1:11–36

Sen R (2008) Biotechnology in petroleum recovery: the microbial EOR. Prog Energ Combust 34:714–724

Seo JY, Kumar RP, Kim B, Seo JC, Park JY, Na JG, Jeon SG, Park SB, Lee K, Oh YK (2016) Downstream integration of microalgae harvesting and cell disruption by means of cationic surfactant-decorated Fe_3O_4 nanoparticles. Green Chemi 18:1–9. doi:10.1039/c6gc00904b

Sharma R, Rawat R, Bhogal RS, Oberoi HS (2015) Multi-component thermostable cellulolytic enzyme production by *Aspergillus niger* HN-1 using pea pod waste: appraisal of hydrolytic potential with lignocellulosic biomass. Process Biochem 50:696–704

Sheng J, Vannela R, Rittmann BE (2011) Evaluation of cell-disruption effects of pulsed-electric-field treatment of *Synechocystis* PCC 6803. J Env Sci Technol 8(8):3795–3802

Shete AM, Wadhawa G, Banat IM, Chopade BA (2006) Mapping of patents on bioemulsifier and biosurfactant: a review. J Scient Indus Res 65:91–115

Sifour M, Al-Jilawi MH, Aziz GM (2007) Emulsification properties of biosurfactant produced from *Pseudomonas aeruginosa* RB 28. Pak J Biol Sci 10:1331–1335

Silva RC, Almeida DG, Rufino RD, Luna JM, Santos VA, Sarubbo LA (2014) Applications of biosurfactants in the petroleum industry and the remediation of oil spills. Int J Mol Sci 15:12523–12542

Singh P, Cameotra SS (2004) Enhancement of metal bioremediation by use of microbial surfactants. Biochem Biophy Res Commun 319:291–297

Sipos B, Szilagyi M, Sebestyen Z, Perazzini R, Dienes D, Jakab E, Crestini C, Reczey K (2011) Mechanism of the positive effect of poly(ethylene glycol) addition in enzymatic hydrolysis of steam pretreated lignocelluloses. C R Biol 334:812–823

Soni SK, Batra N, Bansal N, Soni R (2010) Bioconversion of sugarcane bagasse into second generation bioethanol after enzymatic hydrolysis with-in house produced cellulases from *Aspergillus* sp. S_4B_2F. Bioresources 5(2):741–758

Srivastava N, Rawat R, Sharma R, Oberoi HS, Srivastava M, Singh J (2014) Effect of nickel–cobaltite nanoparticles on production and thermostability of cellulases from newly isolated thermotolerant *Aspergillus fumigatus* NS (class: Eurotiomycetes). Appl Biochem Biotechnol 174:1092–1103. doi:10.1007/s12010-014-0940-0

Stevens CE (1969) In Kirk-Othmer encyclopedia of chemical technology, vol 19, 2nd edn. Wiley, New York, pp 507–593

Suthar H, Hingurao K, Desai A, Nerurkar A (2008) Evaluation of bioemulsifier mediated microbial oil recovery using sand pack column. J Microbiol Methods 75:225–230

Teichmann B, Linne U, Hewald S (2007) A biosynthetic gene cluster for a secreted cellobiose lipid with antifungal activity from *Ustilago maydis*. Mol Microbiol 66:525–533

Toren A, Navon-Venezia S, Ron EZ, Rosenberg E (2001) Emulsifying activity of purified alas an proteins from *Acinetobacter radioresistens*. Appl Environ Microbiol 67:110–1106

Transparency Market Research (2014) Microbial biosurfactants market (rhamnolipids, sophorolipids, mannosylerythritol lipids for household detergents, industrial & institutional cleaners, personal care, oilfield chemicals, agricultural chemicals, food processing, textile and other applications – global industry analysis, size, share, growth, trends and forecast, 2014–2020. Available at: www.transparencymarketresearch.com/microbial-biosurfactants-market.html

Ulloa G, Coutens C, Sánchez M, Jineiro J, Fábregas J, Deive FJ, Rodríguez A, Nuneza MJ (2012) On the double role of surfactants as microalga cell lysis agents and antioxidants extractants. Green Chem 14:1044–1051

Urum K, Pekdemir T (2004) Evaluation of biosurfactants for crude oil contaminated soil washing. Chemosphere 57:1139–1150

Wang H, Mochidzuki K, Kobayashi S (2013) Effect of bovine serum albumin (BSA) on enzymatic cellulose hydrolysis. Appl Biochem Biotechnol 170:541–551. doi:10.1007/s12010-013-0208-0

Wright M, Brown R (2007) Comparative economics of biorefineries based on the biochemical and thermochemical platforms. Biofuels Bioprod Biorefin 1:49–56

Xin L, Hong-ying H, Yu-ping Z (2011) Growth and lipid accumulation properties of a freshwater microalga *Scenedesmus* sp. under different cultivation temperature. Bioresour Technol 102:3098–3102

Yakimov M, Amro M, Bock M (1997) The potential of *Bacillus licheniformis* strains for in situ enhanced oil recovery. J Pet Sci Eng 18:147–160

Yan S, Li J, Chen X, Wu J, Wang P, Ye J, Yao J (2011) Enzymatical hydrolysis of food waste and ethanol production from the hydrolysate. Renew Energ 36:1259–1265

Yan S, Chen X, Wu J, Wang P (2013) Pilot scale production of fuel ethanol from concentrated food waste hydrolysates using *Saccharomyces cerevisiae* H058. Bioprocess Biosyst Eng 36:937–946

Yang X, Lee JH, Yoo HY, Shin HY, Thapa LP, Park C, Kim SW (2014) Production of bioethanol and biodiesel using instant noodle waste. Bioprocess Biosyst Eng. doi:10.1007/s00449-014-1135-3

Yernazarova A, Kayirmanova G, Baubekova A, Zhubanova A (2016) Chapter 5: Microbial enhanced oil recovery. “chemical enhanced oil recovery (cEOR) – a practical overview”,. Ed. Laura RZ, InTech, Rijeka ISBN 978-953-51-2701-7, doi: 10.5772/64805

Ying GG (2006) Fate, behavior and effects of surfactants and their degradation products in the environment. Environ Int 32:417–431

Yoon SH, Robyt JF (2005) Activation and stabilization of 10 starch-degrading enzymes by Triton X-100, polyethylene glycols, and polyvinyl alcohols. Enzyme Microb Technol 37:556–562

Zeng Y, Zhao S, Yang S, Ding SY (2014) Lignin plays a negative role in the biochemical process for producing lignocellulosic biofuels. Curr Opin Biotechnol 27:38–45

Zhang Z, Donaldson H, Ma X (2012) Advancements and future directions in enzyme technology for biomass conversion. Biotechnol Adv 30(4):913–919

Zosim Z, Gutnick DL, Rosenberg E (1982) Properties of hydrocarbon-in-water emulsions stabilized by *Acinetobacter* RAG-1 emulsan. Biotechnol Bioeng 24:281–292

Zulianello L, Canard C, Köhler T, Caille D, Lacroix JS, Meda P (2006) Rhamnolipids are virulence factors that promote early infiltration of primary human airway epithelia by *Pseudomonas aeruginosa*. Infect Immun 74:3134–3147

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