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Review

Plant-Derived Saponins: A Review of Their Surfactant Properties and Applications

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Abstract: In response to increasing natural surfactant demand and environmental concerns, natural plant-based surfactants have been replacing synthetic ones. Saponins belong to a class of plant metabolites with surfactant properties that are widely distributed in nature. They are eco-friendly because of their natural origin and biodegradable. To date, many plant-based saponins have been investigated for their surface activity. An overview of saponins with a particular focus on their surface-active properties is presented in this article. For this purpose, works published in the past few decades, which report better surfactant relevant properties of saponins than synthetic ones, were extensively studied. The investigations on the potential surfactant application of saponins are also documented. Moreover, some biological activities of saponins such as antimicrobial activity, antidiabetic activity, adjuvant potentials, anticancer activity, and others are reported. Plants rich in saponins are widely distributed in nature, offering great potential for the replacement of toxic synthetic surfactants in a variety of modern commercial products and these saponins exhibit excellent surface and biological activities. New opportunities and challenges associated with the development of saponin-based commercial formulations in the future are also discussed in detail.

Keywords: natural surfactants; plants; saponins; *Sapindus mukorossi*; soap nuts; eco-friendly; synthetic surfactants

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1. Introduction

Environmental pollution is one of the great existential global burdens that has degraded the earth's ecosystem and threatened life on earth [1]. In general, a trend can be seen towards using natural products instead of synthetic ones because of environmental concerns [2–4]. It is, however, a challenge for our generation, not just because they are scarce, but also because they are costly to extract and process compared with synthetic alternatives [5]. The synthetic chemical compound known as surfactant falls under the same category. In general, surfactants are known for increasing the cleansing power of water by reducing its surface tension, which makes them a common component of household detergents and cleaning products [6]. As well as being employed in oilfield chemicals, agricultural chemicals, pharmaceuticals, textiles, and polymerization of emulsions used in cosmetics, personal care products, food, and paper processing, they also find application in many other fields [7,8]. Since surfactants are widely used in a wide range of industries, they are among the most produced industrial chemicals. To meet consumer demands, this vast variety of surfactants has been synthesized. Surfactants are largely synthesized from raw petrochemicals [9]. Due to their petrochemical origin, these chemicals are mostly toxic and non-biodegradable, causing a great deal of environmental damage [10,11]. However, natural surfactants are an eco-friendly and sustainable alternative to their synthetic counterparts [11].

In general, natural surfactants are divided into two categories based on their origin: (i) natural surfactants produced by the plants and (ii) substances produced by fermentation of alkanes, oils, sugars, and waste in the presence of microbes (also called biosurfactants) [5,12]. The production of bio-surfactants is more rare because of the high cost of production and threat to food security as it uses carbon sources [6]. There is no doubt that plants are major sources of natural surfactants. Research should therefore focus on exploring, extracting, and isolating natural surfactants from plants that are found throughout nature. Bioactive, biodegradable chemicals are synthesized by plants [13] in an unlimited number, and they are less toxic and harmful than synthetic chemicals.

Plant saponins have the most surfactant properties of all the bioactive chemical compounds [14]. When agitated with water, they form a soapy lather, hence their name "saponins" [15]. They are eco-friendly because of their natural origin, biodegradable and non-toxic which is of utmost importance from environmental and health perspectives. Along with being bioactive, previous works have documented the better physicochemical properties of saponins than synthetic ones. Saponin-rich plants offer excellent physicochemical and biological properties, making them a promising source of natural surfactants, both for research and for commercial purposes [16].

In this review, we provide a brief overview of the molecular and physicochemical properties of plant-based natural surfactants, saponins, emphasizing surfactant properties similar to those of conventional surfactants along with their potential applications. Here, we also discuss the new opportunities, prospects, and challenges associated with the development of saponin-based commercial formulations. Therefore, there is a need for further studies on the development of commercial formulations based on saponins that can replace synthetic counterparts, making more efficient use of organic resources and making a positive contribution towards a greener environment.

2. Molecular Structures of Saponins

It has been noted that saponins are naturally occurring amphiphilic glycosides, which contain polar glycone structure moieties (sugars) separated from nonpolar aglycones structure moieties (also known as sapogenins) [7]. Saponins are classified according to their aglycone counterparts as (i) steroidal saponins and (ii) triterpenoid saponins [17,18]. The difference between these two classes is that the steroidal saponins are molecules with 27 C-atoms whereas the triterpenoid saponins are molecules with 30 C-atoms [8]. Triterpenoid saponins are further subcategorized into (i) oleanane saponins (e.g., *Sapindus mukorossi*, *Camellia oleifera*, etc.) (ii) ursolic acid saponins (e.g., *Ilex paragariensis*) and (iii) dammarane saponins (e.g., *Panax gingseng*). Steroid saponins are also further divided into furostanol type and spirostanol type [9]. Saponins from some families such as Solanaceae have steroidal glycoalkaloids as aglycone backbone [10]. Based on number of sugar units, saponins are classified into (i) monodesmosidic saponins, which have a single sugar unit attached to carbon-3, (ii) bidesmosidic saponins having two sugar units attached to C-3 and C-26 or 28 and (iii) tridesmosidic saponins: a compound that consists of three sugar units attached [19,20]. Branched or linear chains of sugars are attached to the aglycone. These sugar units are mostly composed of D-glucose (Glc), D-galactose (Gal), L-arabinose (Ara), L-rhamnose (Rha), D-xylose (Xyl), D-fructose (Fuc), and glucuronic acid (GlcA) [21,22]. As an example, a photograph of the fruit of *Sapindus mukorossi*, foam obtained after shaking fruit pericarp in water and the structures of main saponins and aglycone are presented in Figure 1.

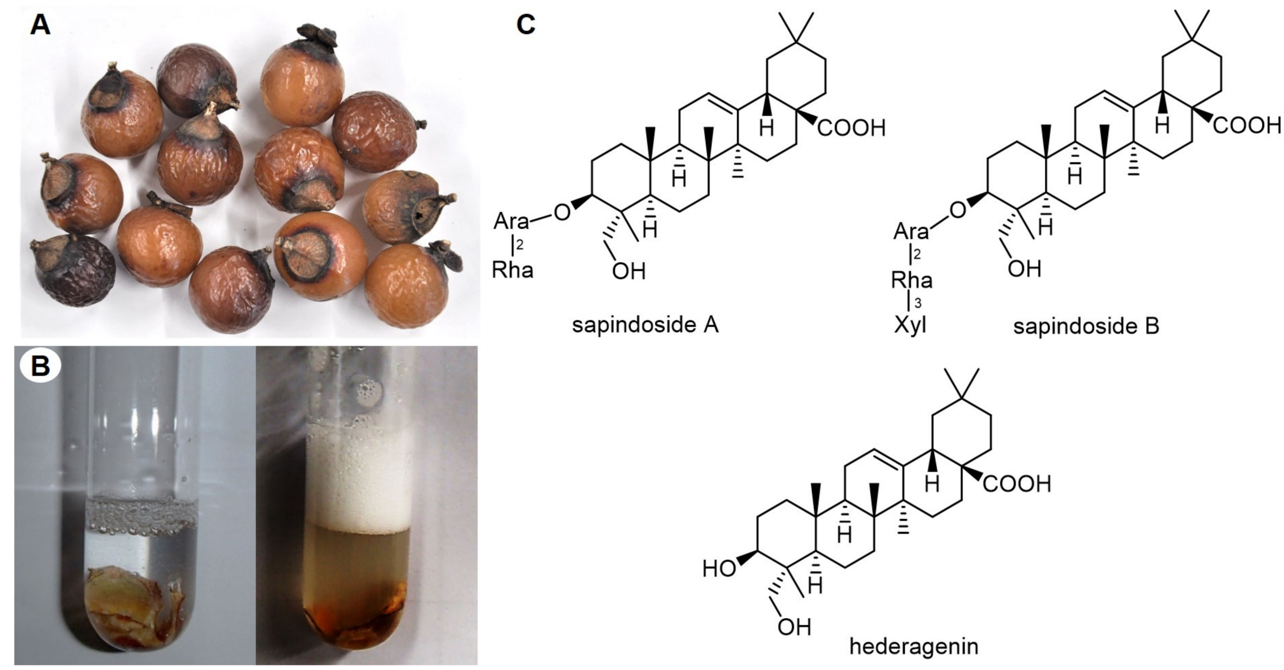

Figure 1. Photograph of *Sapindus mukorossi* fruits (**A**), a foam formed after shaking pericarps in water (**B**), and structures of saponins and their aglycone, hederagenin (**C**).

3. Sources of Saponins

Saponins are a diverse group of secondary metabolites predominantly distributed in more than 100 families of vascular plants including some marine sources. Dicotyledonous plants are the major sources of triterpenoid saponins (families such as Fabaceae, Araliaceae, and Caryophyllaceae) while monocotyledonous plants (families such as Liliaceae, Dioscoreaceae, and Agavaceae) are the major sources of steroidal saponins [2,23]. A list of some saponin-rich plants that are traditionally utilized as natural surfactants is presented in Table 1. Similarly, a list of other plants rich in saponin that could be potential natural surfactant sources is presented in Table 2.

Table 1. List of some common saponin-rich plants traditionally utilized as washing agents.

Scientific Name	Common Name	Saponin Type	Parts Used	References
Acacia concinna	Shikakai	Triterpene	Pods and bark	[24,25]
Acanthophyllum squarrosum		Triterpene	Roots, grooves, shell and white interior.	[13,14]
Albizia procera	Seto Siris	Triterpene	Leaves	[26]
Chlorogalum pomeridia	Soap root	Triterpene	Root	[27–29]
Quillaja saponaria	Soap bark	Triterpene	Inner bark	
Sapindus mukorossi	Soap nut, Indian Soapberry, Ritha, Washnut	Triterpene	Fruit pericarp	
Saponaria officinalis	Soapwort	Triterpene	Roots and Leaves	
Sapindus saponaria	Soap berry	Triterpene	Seed	

Table 2. List of some saponin-rich plants which might act as natural surfactants.

Scientific Name	Common Name	Parts Used	References
Acorus gramineus	Grass-leaved Sweet Rush, Japanese Sweet Flag, Dwarf Sweet Flag	Leaves	[12]
Aesculus assamica	Horse Chestnut	Leaves	[12]
Aesculus indica	Kanor, Indian horse chestnut, Barkhor	Fruits	[18]
Agave americana	Ran Ban, Kantala, Bara Kunwar, Agave	Leaves	[18]
Agave offoyana	Maguey	Flowers and leaves	[30,31]
Agave sislana	Sisal	Leaves	[32]
Allium nigrum	Ornamental onion	Roots and Leaves	[17]
Asparagus adscendens	Saunspali, Sansban	Fruits and roots	[18]
Asparagus racemosus	Shatavari	Roots	[18]
Balanites aegyptiaca	Heglig	Fruits, seeds and bark	[33]
Beaucarnea recurvata	Ponytail palm	Leaves	[17]
Bupleurum chinense	Bei Chai Hu	Roots	[17]
Camellia chekiangoleosa		Seed	[19]
Camellia japonica		Leaf and stem	[19]
Camellia oleifera	Tea	Seeds	[34]
Camellia reticulata		Seeds	[19]
Camellia sinensis	Tea	Root, seeds, leaves and flowers	[18,19]
Caryocar villosum	Piquia	Stems	[17]
Chiococca alba	West Indian milkberry	Roots	[17]
Chlorogalum pomeridianum	Soap plant	Bulbs	[15]
Chlorophytum borivilianum	Safed musli	Leaves	[18]
Cicer arietinum	Chickpeas	Seeds	[20]
Cissus modeccoides		Leaves and stems	[12]
Cissus repen		Stems	[12]
Digitalis lanata	Woolly foxglove	Leaves	[15]
Digitalis purpurea	Purple foxglove	Leaves and seeds	[15]
Dillenia parviflor		Fruits	[12]
Discorea composite	Yams	Rhizomes and roots	[15]
Garcinia	Yellow Mangosteen	Fruits	[12]
Garuga pinnata	Garuga	Leaves	[12]
Glinus lotoides	Soap Jacob	Roots, leaves and seeds	[15]
Glycine max	Soya bean	Sprouts and seeds	[16]
Gypsophilla paniculata	Baby's breath	Roots	[15]
Harpullia austrocaledonica		Bark	[17]
Ilex paraguariensis	Mate	Fruits	[21]
Lens culinaris	Lentils	Seeds	[20]
Lonicera japonica	Honeysuckle	Leaves	[18]
Luffa cylindrica	Sponge Gourd	Fruits	[12]
Microcos tomentosa		Leaves	[12]
Momordica charantia	Bitter melon	Fruits and stems	[17]
Oryza sativa	Asian rice	Peels	[12]
Oxalis corniculata	Creeping wood sorrel	Leaves and stems	[12]
Phaseolus vulgaris	Haricot bean	Seeds	[20]

Table 2. *Cont.*

Scientific Name	Common Name	Parts Used	References
Phaseolus vulgaris	Kidney beans	Seeds	[20]
Pisum sativum	Green pea	Seeds	[20]
Sapindus rarak		Fruits	[12]
Sapindus trifoliatus		Pericarp	[22]
Sesamun orientale	Beniseed	Leaves	[12]
Silene inflata.	Bigru	Roots	[18]
Silphium asteriscus	Starry rosinweed	Leaves and stems	[17]
Solanum xanthocarpum	Yellow-berried Nightshade	Fruits and stems	[17]
Tribulus terrestris	Puncture vine	Fruits	[17]
Trigonella faenum graecum	Fenugreek	Seeds and leaves	[15]
Vigna radiata	Mung bean	Seeds	[20]
Yucca schidigera	Yucca	Bark	[17]
Zephyranthes carinata	Pink rain lily	Bulb	[4]
Ziziphus joazeiro	Juá	Bark	[32]

Saponins are generally found in the roots, leaves, fruit, pericarp, flowers and seeds of a plant [15]. Saponins extracted from a plant are often a blend of various types of saponins [31] The composition and concentration of saponin extracts not only vary in different plants but also in different parts of the same plant. Saponin composition and content is also strongly affected by the environmental factors during the development of the plant and on the extraction procedure [9,15,16].

4. Extraction of Saponins

There are various methods for the extraction of saponins which been extensively researched and well documented [35–40]. The conventional methods for saponin extraction are maceration, Soxhlet extraction, and reflux extraction. These extraction techniques are mainly simple and do not require sophisticated experimental settings. The methodology followed in various published works [41–46] has been summarized here. The extraction of saponins begins with the plant material being shade dried and pulverized into a fine powder. Lipophilic solvents such as petroleum ether or n-hexane are used to defat the powdered plant material. The extraction is then carried out with a solvent that contains 50–98 percent aqueous alcohol (methanol or ethanol). The concentrated saponin-containing aqueous solution is obtained by evaporating the alcoholic crude extract in a rotary evaporator. Using a separating funnel, the aqueous solution is then subjected to solvent-solvent extraction with n-butanol in a 1:3 ratio. The butanol fraction is then thoroughly dried in a rotary evaporator, yielding crude saponin extract to work with.

However, the conventional methods require very large amount of extraction solvents, longer time for extraction and are less efficient in most of the cases. Meanwhile, there have been remarkable developments in the saponin extraction methods by the introduction green technologies (advanced extraction methods) such as ultrasound assisted extraction, microwave-assisted extraction and accelerated solvent extraction [47,48]. In contrast to conventional methods, they require relatively less extraction time, less extraction solvent and have a higher extraction efficiency. Furthermore, this allows for a better and more selective extraction of desired bioactive substance. However, they require specially designed experimental settings which can be expensive during installation but economical and efficient for long run [47]. These techniques are still in the stage of further advancements. Table 3 summarizes technicalities of both the extraction procedures discussed in published articles [38,49].

Table 3. Various methods for the extraction of saponins.

Extraction Method		Extraction Principle	Extraction Solvent	Extraction Temperature	Extraction Time	Extraction Procedure	Advantage/Disadvnatages
Conventional Methods	Maceration	Solid-liquid interface extraction based on the solubility and effective diffusion of desired solute into the solvent.	Water or 50–98% aqueous alcohol (methanol and ethanol)	Varies from room temperature to the boiling point of the solvent used	Varies from few hours to days to weeks	Defatted plant material is soaked in the suitable solvent for desirable period of time. It is sometimes assisted by periodic mechanical stirring.	Longer extraction time. High amount of extraction solvent.Low saponin yield
	Soxhlet Extraction and Reflux Extraction	Extraction by continuous distillation process.	Mostly 50–98% aqueous ethanol.	Heated up to the boiling point of the extracting solvent.	24–72 h for Soxhlet extraction. 1–4 h for reflux extraction.	Extraction process involves heating a solvent to boiling and then returning the condensed vapors to the flask containing plant material resulting in subsequent dissolution of active components. In case of soxhlet extraction, plant material is separately placed in thimble.	Degradation of thermally labile components.
Green Technologies	Ultrasound assisted extraction	Ultrasound radiation disrupts the cell structure and facilitates release of intracellular contents due to mechanical effects of acoustic cavitation in solvents.	Pure or aqueous solvents of ethanol and methanol		10–20 min	Plant material dissolved in the suitable solvent is irradiated through ultrasound radiation.	Higher saponin yield. Relatively short extraction time. Minimum extraction solvent.

Table 3. *Cont.*

Extraction Method		Extraction Principle	Extraction Solvent	Extraction Temperature	Extraction Time	Extraction Procedure	Advantage/Disadvnatages
Green Technologies	Microwave assisted extraction	Absorption of microwave radiation by the water molecules in the plant material disrupts the cell structure which facilitates the release of desired component into solvents	Pure or aqueous solvents of ethanol and methanol		10–20 min	Plant material dissolved in the suitable solvent is irradiated through the microwave radiation (0.3–300 GHz).	Higher saponin yield. Relatively short extraction time. Minimum extraction solvent
	Pressurized solvent extraction	Automated Pressurized solvent extraction.	Water or methanol	Most common operating temperature is 100 °C at 1500 psi	15–25 min	Extraction solvent is pumped through the sample vessel continuously by applying high pressure.	Higher saponin yield. Relatively short extraction time. Minimum extraction solvent.

Psi—Pound per Square Inch, GHz—gigahertz.

5. Surfactant Properties of Saponins and Their Potential Applications

The surfactant properties of saponins in aqueous solutions can be attributed to their amphiphilic structure, which is a combination of lipophilic non-polar aglycone and hydrophilic polar glycone moieties [8]. This structural feature of a saponin molecule resembles that of a synthetic surfactant molecule. A typical surfactant molecule also has an amphiphilic structure with a water-soluble (hydrophilic) head group attached to a water-insoluble (hydrophobic) tail group. The hydrophilic part is a highly polar group (ionic or non-ionic) while the hydrophobic part is a long chain hydrocarbon (aliphatic, aromatic, or the mixtures of both) [50]. Based on the charge on the hydrophilic polar head group, surfactants are classified as (i) anionic Surfactants with a hydrophilic head of the anionic functional group (ii) cationic Surfactants with a hydrophilic head of the cationic functional group (iii) zwitter-ionic Surfactants with a hydrophilic head made of both anionic and cationic functional groups and (iv) Nonionic Surfactants with uncharged hydrophilic head [51]. In the case of a saponin molecule, the hydrophilic part is made up of water-soluble sugar chains while the hydrophobic part may be a water-insoluble steroid or triterpenoid [52]. With this combination, saponins belong to a class of non-ionic surfactants and hence exhibit various surfactant relevant properties (surface activity, micellization, foaming, detergency, wetting, emulsification, etc.) [53]. These are extremely important properties to investigate for the use of saponins as surfactants.

5.1. Micellization Behavior and Reduction of Surface Tension

In an aqueous solution, the surfactant molecules exhibit interesting behavior due to their amphiphilic structure which has been presented with a diagram in Figure 2. They tend to collect on the surface at low surfactant concentrations, with the hydrophilic head orientated towards and the hydrophobic head away from water molecules [4], as shown in Figure 2A.

This phenomenon enhances the surface activity and reduces the surface tension of water. Figure 2B shows how the surfactant molecules remain unassociated until they reach a concentration known as critical micelle concentration (CMC).

Above CMC, the excess surfactant molecules aggregate together to form a cluster called micelles. CMC is the saturation point at which the surfactant-containing aqueous solution acquires the lowest stable surface tension value [42]. Once micelles have formed, there is no significant change in surfactant adsorption at the surface. As a result, any further increase in surfactant concentration does not affect surface tension; instead, it aids in the creation of micelles [43], as seen in Figure 2C.

In Figure 2, water molecules are not included for the clear representation of micelle formation and the phenomenon of surface tension reduction by surfactant molecules. Saponins, due to their amphiphilic nature, exhibit surface-active properties like any other surfactants in an aqueous solution. They also forms micelle above CMC [44] and reduce the surface tension of water accordingly [52].

CMC is an important physical parameter to determine surface-active properties of surfactants. At CMC, various measurable physicochemical properties (such as surface tension, electrical conductivity, refractive index, light scattering, etc.) of the surfactant solution show abrupt change due to which a sharp breakpoint is obtained in the curve when plotted against the surfactant concentration or its logarithm in case of surface tension. CMC values are determined by the point where the two fitted straight lines intersect [54]. This feature has been extensively used in the experimental determination of the CMC of a surfactant solution [50]. The CMC of some saponin-rich plant extracts has also been investigated by various methods. However, the CMC and reduced surface tension values at a given saponin concentration of some saponin-rich solution obtained by tensiometry methods are reported in Table 4. For a comparative discussion, the CMC values along with the reduced surface tension values of some synthetic surfactants mostly used in commercial formulations are also reported in Table 5.

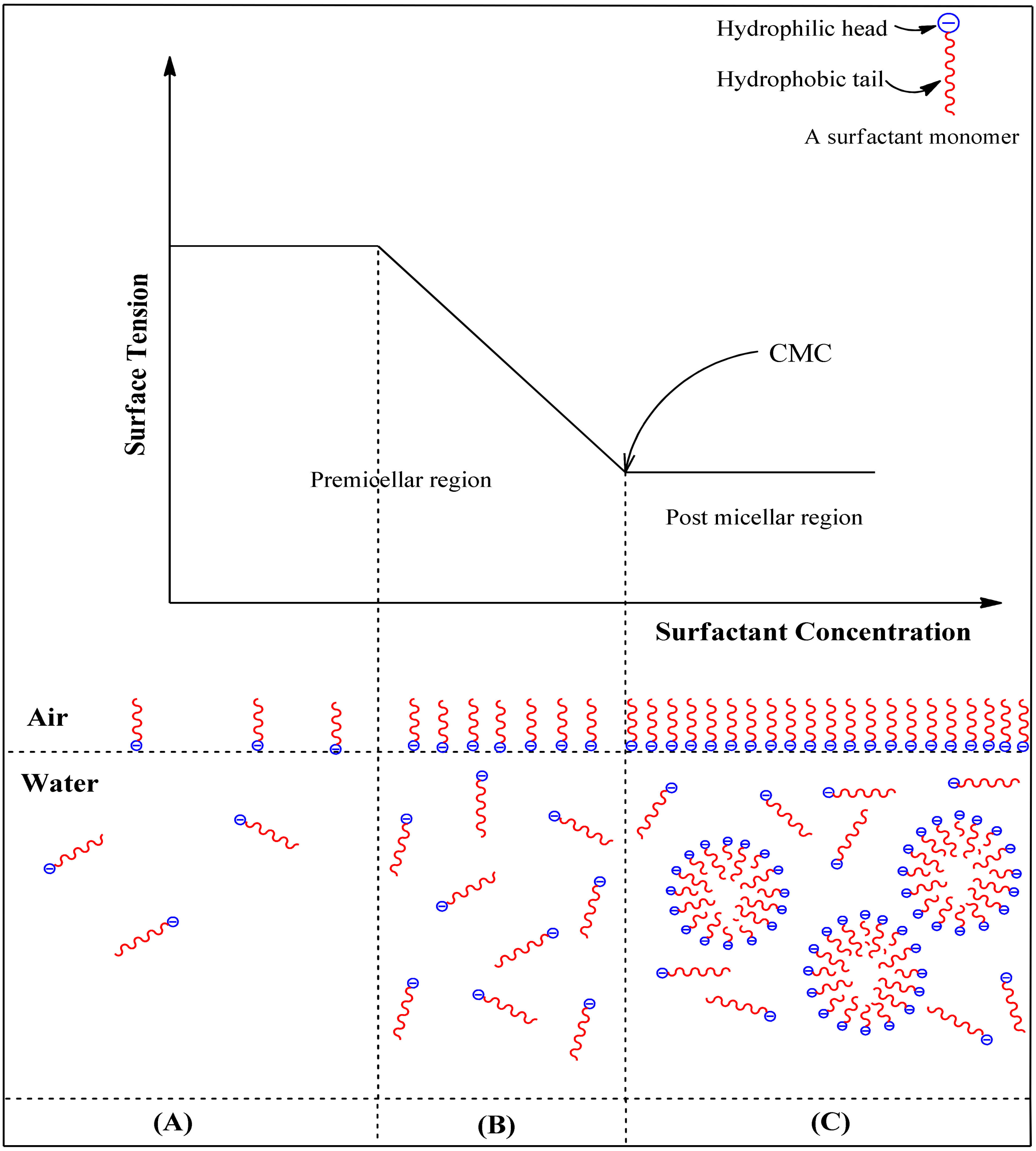

Figure 2. Diagrammatic illustration of micellization behavior of surfactants in aqueous solution. (**A**) At low surfactant concentration, a very less reduction in surface tension is observed. (**B**) With the increased surfactant concentration, surface tension reduces steadily till CMC is reached. (**C**) Beyond CMC, no more changes in surface tension are observed.

Table 4. CMC and reduced surface tension values of aqueous saponin solutions extracted from some plants.

Saponin Sources	Parts Used	CMC (g/cc)	Reduced Surface Tension (mN/m)/[Saponin](g/cc)	Temperature (°C)	References
Acacia concinna	Pods	7.00×10^{-2}	$\approx 32.5/1.00 \times 10^{-2}$	20 ± 2	[45]
	Pods	NA	$35.6 \pm 0.2/1.00 \times 10^{-2}$	25	[55]
	Pericarp	4.6552×10^{-2}	NA	NA	[46]
Agave sislana		6.84×10^{-4}	$(33.57–45.13)/(1.5–4.5) \times 10^{-4}$	25	[32]

Table 4. *Cont.*

Saponin Sources	Parts Used	CMC (g/cc)	Reduced Surface Tension (mN/m)/[Saponin](g/cc)	Temperature (°C)	References
Albizia procera	Leaves	7.00×10^{-3}	$\approx 43.75/1.00 \times 10^{-2}$	20 ± 2	[45]
		NA	$46.6 \pm 0.2/6.0 \times 10^{-3}$	25	[55]
Bellis perennis	Flowers	7.60×10^{-5}	$36.8/7.60 \times 10^{-5}$	20	[53]
Betula pendula	Leaves	2.4×10^{-4}	$45.7/2.4 \times 10^{-4}$	20	[53]
Camellia oleifera	Seeds	NA	$50/5 \times 10^{-3}$	NA	[3]
Equisetum arvense	Haulm	3.30×10^{-5}	$37.9/3.30 \times 10^{-5}$	20	[53]
Genipa americana	Fruits	6.50×10^{-4}	31.39 ± 0.15	25 ± 1	[56]
Hedera algeriensis	Leaves	5.00×10^{-4}	40	20	[57]
Ilex paraguariensis	Fruits	1.4946×10^{-1}	52.8	20 ± 2	[21]
Juglans regia	Bark	8.80×10^{-3}	$\approx 45.00/1.00 \times 10^{-2}$	20 ± 2	[45]
Panax ginseng	Roots	6.27×10^{-4}	NA	25	[32]
Quillaja saponaria		2.84×10^{-4}	NA	25	[32]
Tamarindus indica	Fruits	8.70×10^{-4}	30.02 ± 0.17	25 ± 1	[56]
Sapindus laurifolia	Fruits	1.70×10^{-2}	38.00	NA	[58]
Sapindus mukorossi	Pods	7.50×10^{-3}	$\approx 35.00/1.00 \times 10^{-2}$	20 ± 2	[45]
		7.50×10^{-3}	$35.30/9.50 \times 10^{-2}$	NA	[4]
	Pericarp	4.50×10^{-3}	$\approx 39/4.50 \times 10^{-3}$	25	[59]
Verbascum densiflorum	Flowers	3.55×10^{-4}	$41.5/3.55 \times 10^{-4}$	20	[53]
Zephyranthes carinata	Bulbs	6.40×10^{-4}	$\approx 41.25/1.00 \times 10^{-2}$	20 ± 2	[45]
		6.40×10^{-4}	$40.76/2.05 \times 10^{-2}$	NA	[4]
Ziziphus joazeiro	Barks	1.064×10^{-3}	$(33.94\text{–}46.52)/(0.8\text{–}5.5) \times 10^{-4}$	25	[32]

≈ Approximately equals to. NA Not available, g/cc—gram per centimeter cube, mN/m—milli Newton per meter and °C—Degree Celsius.

Table 5. CMC and reduced surface tension values of some synthetic surfactants in aqueous media.

Surfactant/Nature	CMC (g/cc)	Surface Tension at CMC (mN/m)	Temperature (°C)	References
Cetyl trimethyl ammonium bromide [CTAB]/Cationic	1.131×10^{-3}	NA	25	[59]
	3.53×10^{-1}	33.4	25	[60]
Sodium Lauryl Sulphate/Anionic	2.004×10^{-3}	39.2	20	[53]
Tween 80/Non-ionic	4.42×10^{-5}	44.4	20	[53]
Triton X100/Non-ionic	1.30×10^{-3}	NA	25	[59]
	1.8763×10^{-1}	34.6	25	[61]

It is clear from Table 4 that the CMC of saponins differs depending upon its source. These variations arise due to the differences in the chemical and molecular structures of saponins. Depending on the source, there is the change in the hydrophobicity of the molecules and the sugar chains attached to them which affect the CMC values. In addition, it is also greatly influenced by the methods of saponin extractions and hence results from different methods differ for the same plant. Most of the saponin extracts tabulated in Table 4 showed CMC values lower than that of the synthetic surfactants (Table 5) which is of great importance and utility. In general, the CMC values for saponins are one or two orders of magnitude lower than those for synthetic ones. It is reported that an effective surfactant can reduce the surface tension of water significantly from 72 mN/m to 32–37 mN/m [4,53]. Most saponins extracts reported in Table 4 reduced surface tension to this extent which signifies good surface activity. Reducing the surface tension of water causes it to foam [2]. Saponins are capable of decreasing surface tension and increasing the foamability of aqueous solutions, even at low concentrations [34]. Formation of micelles in aqueous solution and reduction of surface tension are the characteristic features of any surfactants, responsible for its versatile industrial applications such as detergent, foaming agents, emulsifier, solubilizer, etc. [53] (Figure 3) which are discussed briefly in the later sections.

Figure 3. Diagrammatic illustration of potential surfactant applications of saponins as an alternative to synthetic surfactants in diverse fields.

5.2. Saponins as Cleaning and Wetting Agents

Surfactants possess the ability to clean dirt, grime, and grease from the substrate [4]. As a result, they are added as a cleaning agent to a variety of household detergents and personal care products. Such an agent facilitates the removal of dirt from the surface being cleaned that is otherwise insoluble in water. The cleaning action of a surfactant is associated with their abilities to reduce surface tension and form micelles in aqueous media [62]. Above CMC, the micellar aggregates remain suspended in water with the hydrophilic head portions forming the outer shell and the hydrophobic tails forming the core of the micelles. The hydrophobic dirt and oil are trapped within the core by these micellar aggregates and solubilized, and can then be readily washed away by water [63]. The cleaning efficiency of a surfactant is governed by its ability to wet the surface to be cleaned [4]. Wetting is a complex phenomenon associated with the adsorption of the surfactant at the solid–liquid interface, which leads to the decrease in the interfacial tension and enhances the wetting behavior. The application of surfactants as wetting agents finds application in the removal of soil, dye, lubrication, and printing by washing and hence has increased commercial interest. Furthermore, they are useful for controlling the spreading of drops in solid surfaces for industrial and medical applications [64]. Saponins as a substitute to conventional surfactants have been routinely investigated for their cleaning and wetting abilities. Chen et al. reported moderate detergency of *Camellia oleifera* saponins compared to *Sapindus mukorossi* crude saponins, SLS, and Tween 80 [34]. Pradhan et al. reported a comparable cleaning efficiency of *Acacia concinna* saponins to that of commercial baby shampoo, while *Albizia procera* saponins had a lower efficiency [55]. Similar results were obtained for their wetting ability [55]. In another investigation, Pradhan et al. reported a similar trend in cleaning abilities of natural surfactants *Sapindus mukorossi* and *Zephyranthes carinata* and synthetic commercial surfactant. *Sapindus mukorossi* and commercial surfactant showed greater cleaning abilities at a high concentration while *Zephyranthes carinata* was efficient at lower concentration. Furthermore, the least wetting time was reported for commercial surfactant, followed by *Sapindus mukorossi*, which indicated good wetting [4]. The saponins of *Saponaria officinalis* saponins were analyzed for heir potential application in food formulations [65] which are reported to have poor wetting ability [66].

5.3. Saponins as Foaming Agents and Stabilizers

Foaming is an important characteristic of a surfactant solution [43]. Foaming occurs when surfactant molecules partially occupy the liquid surface. In this process, spherical liquid films come out of the surface in the form of foams from areas unoccupied by the surfactant, and thus, with a higher surface tension. Foam production, which is usually a property desired by consumers, has, however, very little to do with the surfactant's cleaning capabilities. Because of their large specific surface area, low specific weight, and ability to create a variety of mechanical properties ranging from liquid to solid, foams are particularly desirable for biomedical and personal care applications [66]. In addition to the rapid foam formation, stable and a satisfactory foaming level is necessary. Thus, commercial formulations frequently incorporate hazardous alkanol amide foam stabilizers. As a result, substitute goods that do not include alkanol amide are required. Most saponins are water-soluble and exhibit foaming properties in an aqueous solution [44]. Monodesmosidic saponins (with one sugar unit) have been reported to exhibit the best foaming characteristics than bidesmosidic saponins or tridesmosidic saponins (with two or three sugar units). Foaming property has been used for the qualitative analysis of saponins in plant extracts. The height and persistence of the froth formed when shaken with distilled water in a test tube determines its presence [15]. Saponins produce not only an adequate amount of foam, but also a stable foam [67]. They do not require additional stabilizers [40]. The excellent surface activity and foaming properties of saponin make it a viable candidate for the development of novel stable foams for biomedical purposes. The foaming strength of a surfactant is measured in terms of its foaming ability. It is determined as the height of the foam determined immediately after foam generation. Foam stability is the measure of the durability of the foam [68]. It is expressed in terms of the R5 parameter defined as the ratio of the foam height after 5 min to that measured in the first stage. Canto et al. reported abundant and persistent foaming ability of *Ilex paraguariensis* saponins. Furthermore, they also reported the diminshed foaming ability of saponins in the presence of electrolytes [21], thereby concluding the significant effect of additives on the foaming ability of saponins. As per the investigation by Tmáková et al. on the foaming ability of saponins extracted from various plants: *Betula pendula* (leaves), and *Sapindus mukorossi* (pericarp) exhibited a good foaming ability while *V. densiflorum* (flowers) showed minimum foaming against the synthetic surfactants SLS and Tween 80. Further, all the saponin extracts reported R5 values of more than 50%, representing good foaming stability comparable to the synthetic ones [53]. Pradhan et al. also a reported a high foaming ability of *Sapindus mukorossi* with the R5 value of more than 60% [4]. Saxena et al. studied the foaming properties of *Sapindus laurifolius* (fruit) and reported the formation of stable foams at high saponin concentration [69].

5.4. Saponins as Emulsifiers

Surfactants are commonly employed for creating and stabilizing emulsion-based products in food, pharmaceuticals, cosmetics, and other industries because of their emulsification properties [60]. Surfactants' amphiphilic nature allows them to adsorb into oil-water interfaces during homogenization, lowering the interfacial tension and resulting in stable emulsions. Natural emulsifiers, according to previous research, are capable of generating a good and stable emulsion. As a result of this research, saponins are now being used as surfactants in the production of oil-in-water emulsions. It has been reported by Tmáková et al. that *Sapindus mukorossi*, *Verbascum densiflorum*, and *E. arvense* saponin extracts are superior to synthetic surfactants (SLS and Tween 80) [53]. Pradhan et al. also reported better emulsification when using natural surfactants derived from *Sapindus mukorossi* and *Zephyranthes carinata* compared to commercial surfactant [4]. De Almeida et al. explored the physicochemical properties of *Genipa americana* and *Tamarindus indica* fruits saponins and a reported good surface activity and emulsifying property for their potential application in oil removal [56]. Saxena et al. studied the emulsification properties of *Sapindus laurifolius* (fruit) and reported the formation of emulsion with maximum stability near CMC [69]. Sabri et al. studied physicochemical properties of triterpene saponins extracted from *Hedera algeriensis* for the formulation of oil-in-water emulsions. The study revealed better stability of emulsions in the presence of a sufficient quantity of saponins [57]. The surfactant property of saponins finds application as emulsifiers in beverages. Saponins derived from *Quillaja* is used in beverage emulsion [70], as model coffee creamers [70], and as effective food encapsulation in forming edible vitamin E [70].

5.5. Saponins as Solubilizers

Surfactants can solubilize organic non-polar compounds (such as petroleum, dye, soil, etc.) in their hydrophobic core [62]. Conventional surfactants have been used in several industrial and environmental processes as solubilizing agents, e.g., processes for removing pollutants from aqueous systems using micellar enhanced ultrafiltration (MEUF) mboxciteB71-sci-1348556,B72-sci-1348556,B73-sci-1348556, surfactant enhance remediation (SER) for soil remediation [74,75], micellar enhanced oil recovery (MEOR) process for higher oil recovery [76], solubilization of hydrophobic dyes in dying as well as dye removal processes [77], and solubilization of hydrophobic drugs [78]. However, with the increasing threat of synthetic surfactants on the environment, saponins as a natural surfactant have attracted researchers' interest in these areas as well, some of which is reported here. Roy et al. investigated saponins obtained from the fruit pericarp of *Sapindus mukorossi* for soil washing applications and were found comparable to that of typical commercial surfactants [79]. Chhetri et al. studied *Sapindus mukorossi* (pericarp) extract for enhanced oil recovery. The investigation reported that the extract significantly reduced the interfacial tension and presented its great potential for enhanced oil recovery [11]. Similarly, Samal et al. also reported positive results for the solubilization of dyes (methylene blue/cationic and eosin yellow/anionic) by the saponins extracted from the fruit pericarp of *Sapindus mukorossi* [80]. Vinarov et al. studied solubilisation of hydrophobic drugs by 13 different saponin extracts and found more improved solubilisation of danazol and fenofibrate in the presence of *Quillaja saponaria* and *Camellia oleifera* than Brij-35 [67].

5.6. Saponins in Commercial Formulations

As the herbal extracts are supposed to be good alternatives for the chemical preparations, various investigations have been carried out to develop personal care products, especially shampoo that is based on naturally derived ingredients. Some of these are reported here. Mainkar and Jolly investigated the assessment of commercial herbal shampoos using surface tension, foaming test, wetting test, and other criteria. The findings of these tests provided insight into the criteria a laboratory-formulated shampoo should meet to be comparable to commercial shampoos [81]. In another investigation, authors attempted to formulate completely natural shampoo with saponins obtained from the pericarps of *Sapindus mukorossi* and alkylpolyglycoside as a major ingredient. The formulations so prepared presented detergency, surface tension, pH and other parameters comparable to that of commercial ones, implying the possibility of formulating completely natural shampoo which was otherwise considered a challenging task [82]. Aghel et al. conducted a study intending to completely replace harmful ingredients in shampoo formulations.

Instead, they assessed the physicochemical, rheological, and organoleptic behaviors of saponins isolated from the roots of *Acanthophyllum squarrosum* as a substitute. The final formulation was found to be desirable, with great cleaning performance and steady foaming ability, and was proposed as a replacement for numerous hazardous surfactants and foaming agents [14]. Nizioł-Łukaszewska et al. evaluated three saponin-containing plants (*Glycyrrhiza glabra*, *Viola tricolor*, and *Solanum dulcamara*) in the context of multifunction cosmetics materials. Saponins were added to the body wash gel formulations to enhance their rheological and foaming properties, as well as to reduce the chance of skin irritation. It is based on these findings that saponins can be classified as safe ingredients in cosmetics formulations [83]. Recently, Moghimipour et al. also formulated synthetic surfactant-free shampoo, saponins from roots of *Acanthophyllum squarrosum* being the major ingredients. The resulting mixture likewise demonstrated good cleaning capabilities, had a pH value within an acceptable range and was deemed suitable for usage [13].

5.7. Other Applications of Saponins

Apart from the potential surfactant application, saponins find a broad spectrum of potential applications ranging from the pharmaceutical industry to food and cosmetics. The pharmaceutical applications can be attributed to their antimicrobial, antioxidant, anti-inflammatory, antidiabetic, anticancer, cholesterol-lowering properties, and hemolytic activities that add to the immune response of the organisms [84,85].

The antimicrobial activity of saponins from various plant sources against various bacterial and fungal strains is well documented. Quinoa saponins extracted from the husks of *Chenopodium quinoa* are reported to pose antibacterial property against *Staphylococus aureu*, *S. epidermidis* and *Bacillus cereus*, causing severe damage through bacterial cell wall degradation followed by disruptions of the cytoplasmic membrane and membrane proteins [86]. Similarly, an antifungal activity of *Ziziphus joazeiro* (bark) saponins has been reported against *Candida albicans* and *Aspergillus niger* [32]. The antioxidant properties of saponins from Camellia roots [84], and seed cakes [85] steroidal saponins from *Agave sisalana* and triterpenic saponins from *Ziziphus joazeiro* [32] have also been reported. Several other studies focused on the antidiabetic property of saponins as well because of their ability to reduce the increased blood plasma glucose, e.g., saponins from *Panax notoginseng* [87,88] and *Entada phaseoloides* (seeds) [89]. Similarly, the hypoglycemic and hypolipidemic activities of total saponins extracted from the stems of *Stauntonia chinensis* in diabetic mice opened up the possibility for its utilization in the treatment of type-2 diabetic [90].

It is reported that the saponin fractions from the seeds of *Chenopodium quinoa* (seeds) [91] and *Bupleurum chinense* (roots) [92], respectively helped boost the immune response and hemolytic activity of mice against ovalbumin. Several other studies on hemolytic activity with the immunological adjuvant property of saponins have been reported from *quillaja* saponins [93], soya saponins [94], Japenese ginseng saponins [95]. Fraction enriched in saponin from *Silene vulgaris* has been reported to pose in vitro hemolytic activity in sheep, although less effective than that of *Sapindus mukorossi* and *Chlorophytum borivilianum* [96]. Recently, the anticancer activity of both triterpenoid and steroid saponins has gained much attention [97–101].

Because of their intense sweetness, some saponins are also used as natural sweeteners in foods and herbal medicines. Due to the sweetness of licorice saponin, i.e., glycyrrhizin, the roots of *Glycyrrhiza inflata*, *G. glabra*, *G. aspera* and *G. uralensis* are widely used in various traditional medicines and also as flavoring agent in foods [70].

6. Conclusions, Challenges and Future Perspectives

As environmental awareness grows, more and more natural products are being used as substitutes for synthetic products all over the world. The raw materials for the synthetic surfactants are mainly petrochemicals. As a result of their petrochemical origin, most of these products are toxic and non-biodegradable, causing harm to the environment. Unlike synthetic surfactants, natural surfactants are derived directly from nature, i.e., from plants or animals. The utilization of natural surfactants helps in reducing the environmental pollutions caused by the extreme application of synthetic surfactants in diverse fields. Therefore, natural surfactants distributed widely in nature should be explored, extracted, and isolated more extensively. Thus, future investigations should focus on the identification of some more plant-based natural surfactants.

A greater number of bioactive chemical substances are synthesized by plants that are biodegradable and less toxic compared to synthetic ones. The saponins derived from plants are among the bioactive chemical compounds that have surfactant properties. Plants rich in saponins are important sources of natural surfactants due to their excellent physicochemical properties and biological properties, both for research and for commercial purposes. There are over 100 families of vascular plants, including some marine ones, that produce saponins. Thus, the development of commercial formulations based on saponins could replace synthetic counter parts completely and contribute to the global green agenda, as better use of plants sources would be made possible. Typically, saponin molecules consist of a hydrophilic part composed of sugar chains and a hydrophobic part composed of steroids or triterpenoids. This combination makes saponins a class of non-ionic surfactants, with various surfactant-relevant properties (reducing surface tension, micellization, foaming, cleaning, dilution, wetting, stabilizing, solubilizing, emulsification, etc.) for wide utilization everywhere. Thus, we can conclude that saponins obtained from plants can be a sustainable and eco-friendly alternative to synthetic surfactants.

As saponins have gained popularity in the scientific community as a sustainable alternative source of natural surfactants, one key focus has been shifted towards utilizing them in diverse fields of application over synthetic ones. It has been further supported by the growth of consumer demands and restrictive environmental legislation. This has encouraged manufacturers to develop more herbal products. Currently, due to limited choices, most of the available products rely on the conventional synthetic surfactants, and the herbal ingredients if added, are mainly for aesthetic purposes. This is because developing commercial formulations completely based on natural raw materials is considered a challenging process. It is a challenge to find materials that can be rationally justified as natural and formulate them into products that function as effectively as synthetic materials. To change consumer perceptions of herbal products, a more radical approach is needed to popularize natural surfactants, emphasizing their safety and efficacy. Educating consumers is also an important role for formulators about the potentially hazardous consequences of synthetic goods and other chemical additions. Further, the extraction and processing cost of the natural surfactants to the final product is comparatively more expensive than the synthetic ones. As a result, although safe and free of adverse effects, these products do not enjoy market popularity. Hence, another significant challenge to overcome is the introduction of saponins as low-cost alternatives. Thus, simple and cost-effective extraction processes have to be developed to commercialize them. These exciting challenges exist for both the production of saponins-based commercial formulations and conducting application-oriented research on saponins. Many saponins such as steroidal glycoalkaloids are toxic when ingested thus great care should be taken when handling these saponins and plant materials which are non-toxic should be selected for the commercial purposes as surfactants.

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