cosmetics

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Review

Hair Care Cosmetics: From Traditional Shampoo to Solid Clay and Herbal Shampoo, A Review

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Abstract: Hair is an important part of the body appeal and its look is a health indicator. Accordingly, recent advances in hair science and hair care technologies have been reported in literature claiming innovations and strategies for hair treatments and cosmetic products. The treatment of hair and scalp, primarily, involved the use of shampoo for an effective, but gentle cleansing; however, for years, the shampoo is considered not only as a cosmetic product having the purifying purpose, but it is also responsible for maintaining the health and the beauty of hair, imparting gloss and improving manageability. For meeting the needs of a multitasking formulation, following also the recent marketing-trend addressed to the "natural world", new challenges for cosmetic technology are aimed towards the research of natural ingredients, as well as new techniques for shampoo formulation. Regarding the recent development of solid shampoos, little information is available about their use, formulation and advantages. This review is largely focused on the description of solid shampoos, mainly based on the use of clays, herbs or flours as washing bases alternative to the traditional ones, consisting of a combination of synthetic surfactants, together with other usual ingredients expected in a shampoo formulation.

Keywords: hair anatomy and physiology; hair care cosmetics; solid clay shampoo; rhassoul clay; herbal shampoos

1. Introduction

As far back as ancient time, people use natural extracts and resources for health care and cosmetic purposes. Accordingly, nowadays, consumers' demand for natural ingredients and additives, especially in cosmetic products, as a replacement of synthetic compounds, having possible negative effects on health and the environment, is tremendously increased. Therefore, with the aim to satisfy these requirements, together with the impelling need for reducing the microplastic use, marketing trends are developing towards a cosmetic based on natural ingredients, generally associated with a healthy lifestyle, both in food and cosmetic fields (i.e., hair care) [1,2]. Moreover, nonetheless, the difficulties due to technologies related to allowed ingredients and their legislative range of concentrations, the cosmetic expertise is focused on the research of raw materials, innovative strategies and techniques for the formulation of novel products, characterized also by a good texture and skin feel [3]. Interestingly, besides the development of products mainly devoted to skin care, several cosmetic industries are focusing on hair care, with the production of safety products and eco-friendly packaging, paying attention to their action. Indeed, for example, in recent literature, the ethnicity appears as an important key factor to take into account in the clinical observation, management, and treatment of skin and hair disorders [4,5].

About this concern, the hair care products evolution, having the main need to act for cleaning the scalp and hair, has brought to wide-ranging types of shampoos. Among them, more recently, powder shampoos and solid shampoos [6], as alternatives to the traditional ones, have appeared, with very interesting advantages. For example, in the traditional shampoos, for a long time, Sodium Dodecyl Sulfate (SDS) was used as a traditional surfactant [7], and now it has been rapidly replaced by herbs, flours and washing clays from the mineral world. Thus, with regard to this aspect, the cosmetic products regulatory agencies (such as CIR, SCCS, ECHA, EFSA) have to pay much more attention to evaluating the toxicity of raw material.

In agreement with the current trend, the cosmetic research for hair care has been focused on the development of solid shampoos from natural ingredients, also as an alternative and eco-friendly packaging way. In fact, among the various advantages of solid shampoos in comparison with the traditional ones, it should be considered, for example, a longer life time and the property of being a handy product, so easy to transport. This indicates also that the associated costs, especially those related to the packaging, are lowered in accordance with the market and consumers' requests.

On this ground, in this review, the attention has been focused on the knowledge of hair care, discussing the important role of traditional shampoos and conditioners, compared with the solid ones. Moreover, since there is little information in literature, the review should also be considered as a presentation of the uses and potential formulations of solid shampoos, in order to provide some guidelines about the development of new products starting from natural ingredients, such as clays and herbs. About the former, a deeper investigation has been performed, presenting the advantages related to the wide-ranging use of clay minerals in solid shampoo formulations. In particular, Rhassoul clay has been discussed for hair care. A brief discussion has also been centered on the safety of these products with the related toxicological evaluation.

2. Hair

2.1. Hair Structure

Hair, protective appendages on the body and structures of integument with sebaceous glands, sweat glands and nails are considered an important part of the body, derived from the skin ectoderm. They are also known as epidermal derivatives, since they originate from the epidermis during embryological development [2]. As described by Naizet [8], the hair is mainly constituted by three parts: the bulb, the root and the stem, and it is implanted in the pilosebaceous follicle in the dermis. The bulb is the deepest end of the hair and is also the portion that makes it grow. It is connected to the richly innervated and vascularized dermal papillae, which allow the contribution of nutrients necessary for hair growth [8]. The root is firmly fixed in the hair follicle, the part of the hair located between the bulb and the surface of the epidermis where hair takes the form of the stem. The root and stem are made of the same three concentric layers: the medulla, the cortex and the cuticle on the outside (Figure 1). The medulla is the central core. The next stratum, the cortex, represents the largest and thickest part of the hair determining many of their mechanical properties [1,8,9]. The cortex is made of packed spindle-shaped cortical cells, filled with keratin filaments parallelly oriented to the longitudinal axis of the hair shaft, and of an amorphous matrix of high sulfur proteins (Figure 1) [10]. In particular, cysteine residues in adjacent keratin filaments tend to form covalent disulfide bonds with a strong crosslink between adjacent keratin chains [9]; thus, it contributes to providing the shape, the stability, and the texture of the hair [9]. The cuticle is a very resistant layer of overlapping dead cells that form a protective barrier against the outside environment and external aggressions. It consists of endocuticle and exocuticle [10]. Normal cuticles have a smooth appearance, allowing light reflection and limiting friction between the hair shafts. Indeed, it is responsible for the hair luster and texture.

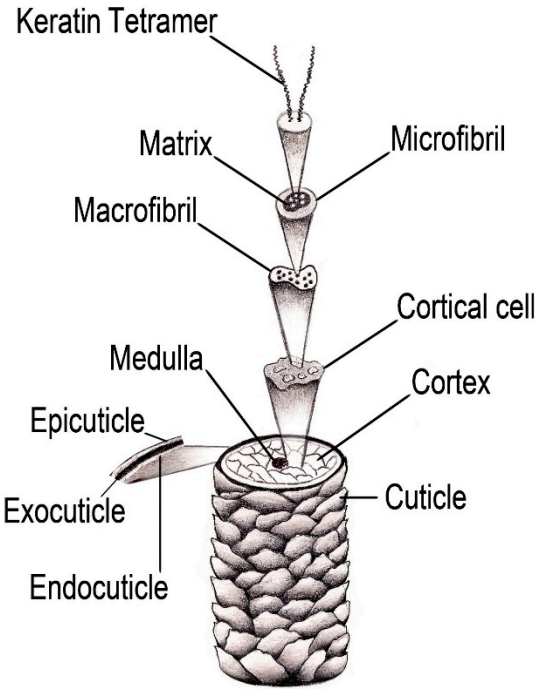

Figure 1. The hierarchical structure of hair.

The cuticle comprises three parts: b-layer, a-layer, and epicuticle [9]. Specifically, described by Hordinsky et al. as well [9], the epicuticle is a hydrophobic lipid layer, made of 18-methyleicosanoic acid on the surface of the fiber, or the f-layer, overlapping cuticle cells surrounding the elongated polyhedral cortical cells. The combination of the outer hydrophobic layer with the cortex gives the physical properties of shine and volume (body), essential for the appearance of "healthy hair". Indeed, if hair is damaged by frictional or chemicals forces with the subsequent removal of the f-layer, the first hydrophobic defense, the hair fiber becomes much more fragile [9]. It is useful to remember that hair fibers contain sulfur-rich proteins, lipids, water, melanin, and trace elements [9].

Keratin is the main component of the hair. It is a fibrous and resistant protein, whose amino-acidic chains are organized in an α helix and contains mainly tyrosine, glycine and cysteine. It is usually present as acidic, neutral and basic keratin [1,9,10].

2.2. Hair Care

If, on one hand, hair texture and shine are usually related to hair surface properties, on the other hand, the integrity of hair is due to the hair cortex [11]. For this purpose, hair products that improve the structural integrity of hair fibers and increase tensile strength are available, along with products that increase hair volume, reduce frizz, improve hair manageability, and stimulate new hair growth [11]. Interestingly, modern cosmetic products are formulated to clean hair from detritus, and to restore and improve hair physiology. For example, intensive conditioning agents can temporarily "replace" the f-layer, improving the moisture retention in the cortex and rebuilding some of the reduced physical properties of hair. Therefore, the boost in hair shine is a key benefit of modern products [11].

3. Shampoos

3.1. Traditional Shampoos

The most common hair care cosmetic product is the shampoo. Arora et al. [2] reported that a shampoo can be described, primarily, as a cosmetic preparation, packed in a form convenient for use, generally applied for cleaning hair and scalp from dirt, residues of previously applied hair styling products and environmental pollutants. In order to maintain the physiological balance of hair essential elements, to leave hair glossy for beautifying them and improving their aesthetical appeal, the cleaning process should be mild. A shampoo should also be easy to remove through rinsing with water, it should produce a good amount of foam to satisfy the expectations of the users (although the foam is not a guarantee of cleaning), and it should be non-toxic and non-irritating for hair and scalp, avoiding any side effects or skin and eye irritation [12]. Among commercial shampoos, besides "normal" cleaning and conditioning hair shampoo, there are "specific" shampoos that have additional functional ingredients considering some hair problems. Indeed, nowadays, shampoo is well beyond the stage of pure cleaning agents of the hair. In detail, these "specific" shampoos contain antibacterial agents, natural essential oils or extracts for treating dandruff, dermatitis and other hair diseases [1,10]. Since the scalp is considered as the most absorbent part of the body, the applied cosmetic products go directly into the blood. Therefore, it is very important to know the effects of ingredients used in shampoo formulations [2]. In the work of Zhang et al. [10], due to the multitude of purposes of these hair care products, ingredients with many effects on hair are listed. In particular, a typical shampoo usually contains a mix of primary and secondary surfactants for cleaning, viscosity builders, solvents, conditioning agents, pH adjusters and other components such as fragrance and, eventually, color for commercial appeal [10]. As for "specific shampoo", there are also many categories of shampoo for different hair targets [13]: shampoos for "normal hair", "dry hair" and "oily hair". "Normal hair" shampoo, containing SDS (named also sodium lauryl sulfate) as the main detergent, provides a good cleaning of the scalp. This type of shampoo is also used for non-chemical treated hair. However, shampoos for "dry hair" ensure mild cleaning and excellent conditioning, by using amphoteric and anionic (i.e., sulfosuccinate) detergents. Moreover, these products are considered suitable for chemically damaged and frequently washed hair. Finally, for "oily hair", characterized by a significant sebum production, shampoo formulations may also contain SDS or sulfosuccinate detergents that, however, could dry hair fibers [9].

From a chemical and of formulation point of view, shampoos are mainly made of washing bases, a mixture of surfactants having cleaning properties to remove dirty and dust from the scalp and hair. The presence of this mixture improves the products' performance, reducing the strong effect of a single surfactant. In particular, detergents can be classified as anionic, cationic, amphoteric and nonionic surfactants according to their chemical moieties [9].

- Anionic surfactants are characterized by a negatively-charged hydrophilic polar group. Among them, ammonium lauryl sulfate, sodium laureth sulfate, sodium lauroyl sarcosinate, SDS, alpha-olefin sulfonate and ammonium laureth sulfate can be cited (Figure 2). Anionic surfactants are very good in removing sebum and dirt; however, they are strong cleaners and may induce an increase of the electrical negative charges on the hair surface, creating frizz and friction. Therefore, in order to reduce damages and to have a mild detergency, secondary surfactants such as nonionic and amphoteric surfactants are usually added in the formulation [4].

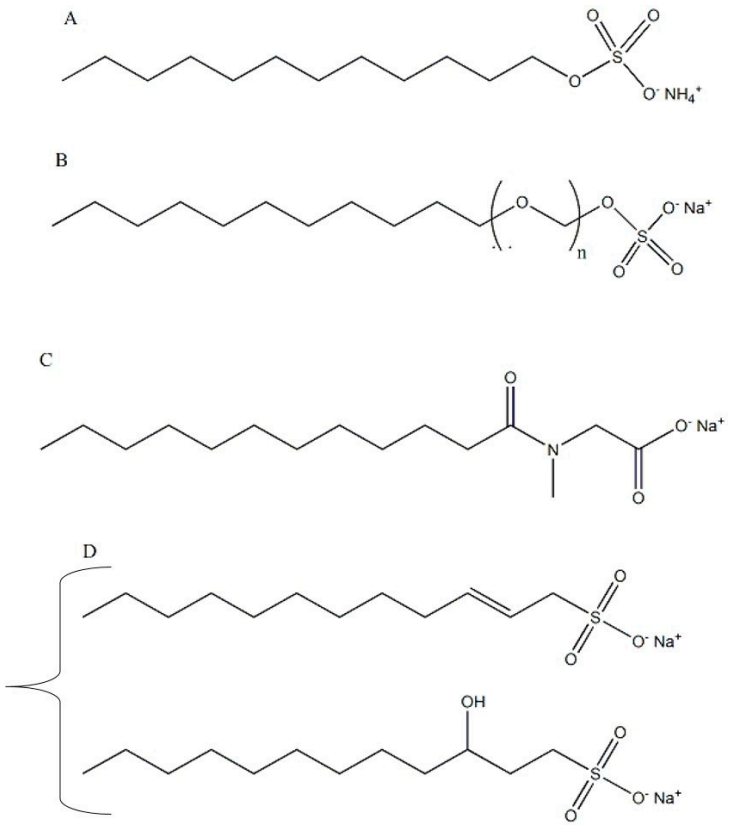

Figure 2. Structure of some anionic surfactant using the example of the C12 chain length representatives: (**A**) Ammonium lauryl sulfate; (**B**) Sodium laureth sulfate; (**C**) Sodium lauroyl sarcosinate; (**D**) Dodecyl alpha olefin sulfonate, Sodium salt.

- Cationic surfactants have a positively charged hydrophilic end are used mainly as conditioners, being able to balance hair negative charges after washing, reducing frizz. Indeed, they are efficient softeners and substantive for hair because of the hair's low isoelectric point (pH 2.15–3.17) [14]. Typical examples are trimethylalkylammonium chlorides, benzalkonium chloride or bromide, and so on (Figure 3) [4]. Due to their chemical nature, they also have bacteriostatic properties [4].
- Amphoteric surfactants are characterized by the charge control through the solution pH values. In other words, they are anionic or cationic surfactants in alkaline or acid solutions, respectively. They are considered very mild and thus dermatologically compatible. Furthermore, they have a good foaming, detergent and wetting properties. For these reasons, they are used to reduce the aggressiveness of anionic surfactants. Two types of amphoteric compounds can be mentioned: alkyl iminodipropionate and (amido) betaines (Figure 3) [4].
- Nonionic surfactants not exhibit electric charge in aqueous solutions due to the absence of hydrophilic dissociable groups. They are less aggressive than other surfactants and, thanks to their eudermic properties, are widely used as emulsifiers and solubilizers in cosmetic formulations. They are often derived from plants, such as glucosides, citrates, sulfosuccinates and hydrolysates proteins. Alcohols, having long chains, exhibit some surfactant properties. Among these, the fatty alcohols, cetyl alcohol, stearyl alcohol, and cetostearyl alcohol (consisting predominantly of cetyl and stearyl alcohols), and oleyl alcohol are very important (Figure 3) [4].

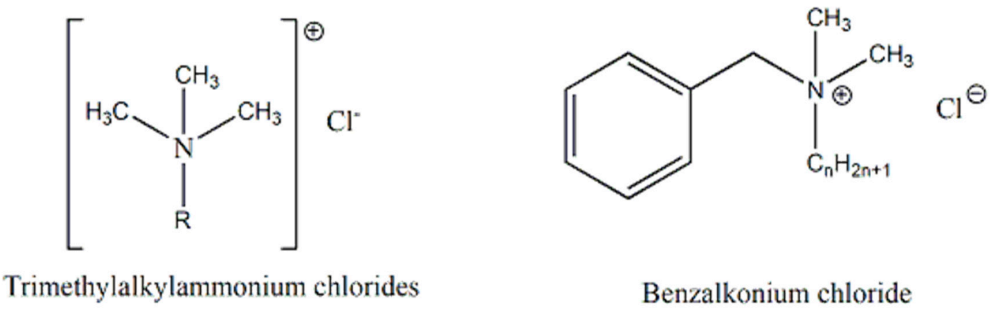

Figure 3. Chemical structure of some examples of cationic surfactants.

As other ingredients in a shampoo formulation, there are substances needed to ensure a suitable consistency of the product, to guarantee stability over time and to improve the pleasantness. Considering the high-water content in the shampoo, the addition of preservatives, to avoid bacterial growth, is needed. Furthermore, there are also: thickeners such as electrolytes, cellulose derivatives, natural gums that increase the consistence of the final product; pH-regulators for adjusting the shampoo pH-values, adapting it to the natural hair and scalp pH (5.5–6.0); and sequestrant agents (EDTA). Perfumes and dyes are added, among the main ingredients, for improving the shampoo sensorial profile [15].

Other important functional ingredients characterize the shampoo and make it suitable for a particular type of hair, taking into account its physiological needs [15]. For example, the presence of specific conditioners transforms the hair care cosmetic in a 2-in-1 product. Therefore, the hair conditioner is another hair cosmetic product very important for hair care. In fact, in order to ensure the hair smoothing for combing, conditioners are necessary.

Generally, conditioners may prevent static electricity, improve the shine and increase the hair protection [10]. In this regard, Hordinsky et al. [9] indicate conditioners as agents able to reduce static electricity between fibers by depositing charged ions on the hair, at least neutralizing the electrical charge. Moreover, they can improve hair shine usually related to hair shaft light reflection. There are several hair product types including instant, deep, leave-on and rinse conditioner. If an instant conditioner aids with wet combing, a deep conditioner has to be applied for 20–30 min and is used for chemically damaged hairs. A leave-on conditioner is applied to towel dried hair and facilitates combing. Instead, a rinse conditioner is used after the shampoo for disentangling hair fibers.

Hordinsky et al. [9] report other four categories of conditioners: film formers (polymers), protein-containing (hydrolyzed proteins), cationic detergents (quaternary ammonium compounds), silicone (dimethicone, ciclomethicone). The film-forming conditioners are used as coating fibers with a thin polymer layer. Protein-containing conditioners are characterized by small proteins with a molecular weight ranging from 1000 to 10,000 Da that penetrate hair shaft, temporarily increasing the fiber strength. Quaternary ammonium compounds induce a thin film formation on hair, helping manageability and even shine. Silicone conditioners reduce the static electricity and friction [9].

3.2. Non-Traditional Shampoos

Preethi et al. [12] defined a shampoo classification, listing different types of products: powder shampoo, liquid shampoo, lotion shampoo, solid gel shampoo, liquid herbal shampoo, solid cream shampoo and aerosol foam shampoo [12]. Among them, in this review, the attention has been focused on solid shampoo and herbal shampoo, reporting the main important information known in literature [12] and the novelty introduced by a clay shampoo.

3.2.1. Herbal Shampoo

Since ancient times, people have been using herbs and herbal extracts for cleaning, beautifying and managing hair. Nowadays, in accordance with an actual trend, cosmetic products formulated with natural ingredients are starting to be used again [16,17].

The interest towards the herbal products is also justified because, on one hand, they are considered less expensive; on the other hand, they present negligible side effects [17], as confirmed in literature in the toxicological studies reported by Middha et al. [18]. In fact, the authors performed the in vivo toxicological estimation in order to evaluate the effects of the extract, the object of study (*Emblica officinalis* Fruit Extract), on cells. The LD_{50} was measured to check lethal toxicity, and it was found to be 1125 mg/kg. In particular, the treatment, by using the extract at a dose of 200 mg/kg and 400 mg/kg to their respective group of mice, for one month, did not show toxic side effects. The selection of these two doses was based on an initial toxicity study where, until one month after administration of the extract, the animals were healthy without any visual signs or symptoms of illness [18].

Interestingly, there is a large number of plants having beneficial effects on hair and being commonly used in shampoos for their content of vitamins, amino acids, sugars, glycosides, phyto-hormones, bioflavonoids, fruit acids and essential oils [2]. Accordingly, various studies on shampoos based on natural ingredients have been developed. In particular, these products must be safe and efficient for long-time use [17], assuring mild detergency and an aesthetic appealing. However, the formulation of cosmetics using natural raw material is a difficult task, since the main challenge regards the selection of these natural ingredients and new formulation techniques [3].

In this regard, Bellare et al. [3] reported as commercially available herbal shampoos, both liquid and powder, are still based on synthetic functional ingredients, boosted with natural raw materials or extracts [2]. As reported in several Indian literature studies [17], herbal shampoos are usually formulated incorporating some common traditional drugs normally employed for hair washing by Indian people [17,19]. Although these plant products can be used either in their powdered form, crude form, purified extracts, or derivative form [2,18], the preparation of an herbal shampoo using only natural materials (milder and safer than the synthetic ingredients), able to compete with traditional shampoos in terms of foaming, detergency and solid content, ends up being very difficult [17].

Al Badi et al. [17] formulated herbal shampoos mainly using the pericarp of *Sapindus mukorossi*, commonly known as Soapnut or Reetha, the fruits of *Phyllanthus emblica* (Amla), and dried pods of *Acacia concinna* (Sheekakai), that have been traditionally used in India for centuries to wash hair [17]. Authors described the formulated herbal shampoo being evaluated for conditioning performance by administering a blind test to 20 student volunteers. The shampoo formula showed good cleansing and detergency, low surface tension, small bubble size and good foam stability after five minutes. Furthermore, several tests were performed to evaluate and compare successfully the physicochemical properties of both prepared and marketed shampoos [17].

Thanks to their high content in saponins, Reetha and Sheekakai ingredients produce a rich lather when shaken with water, also giving advantageous effects on skin that make them important ingredients for cosmetic applications [20]. In addition, Reetha, Amla and Sheekakai are each characterized by peculiar properties. For example, the Amla extract, nourishing hair, can help hair growth and, thanks to the presence of fatty acids penetrating through the scalp, can remove dryness and dandruff, while its antioxidant properties strengthen hair roots [21]. Reetha, instead, among all its properties, could be considered a mild cleansing agent, which, thanks to its antimicrobic properties, can remove any microorganism responsible for infections. Furthermore, it makes hair shine, restoring the natural hair texture. [21] About Sheekakai, it is reported that it retains the natural oil of hair, keeps hair lustrous, reduces hair loss, adds volume, gives hair strength, and is a powerful antidandruff and conditioning agent [21].

Other common herbal ingredients used for shampoo formulation are: *Azadirachta indica* (Neem) as antibacteric, *Ocimum sanctum* (Tulsi) that contains vitamins, antioxidants, oligoelements, having

also antibacterial properties, *Aloe vera* (aloe) as conditioning agents, *Terminalia chebula* (harda, haritaki) and *Terminalia bellirica* (bahera), with proven efficacy in preparation for hair care [17].

Utane et al. [21] also reported that Nagarmotha (*Cyperus Rotundus*) promotes hair growth, Bhringaraj (*Eclipta prostrata*) rejuvenates the scalp, Brahmi (*Bacopa monnieri*) nourishes hair and helps with better circulation on the scalp. The appropriate pH of shampoo also helps in minimizing eye irritation, enhancing hair wellness and maintaining the physiology of the scalp [2,17,22].

In accordance with the quality and security of the products, when commercial shampoos are compared with those formulated in laboratory (also in solid form), specific parameters must be evaluated. For this purpose, when herbal-based shampoos are taken into account, special tests, reported in Table 1, need to be performed [2,16,17,22].

Table 1. Physicochemical properties of commercial or prepared herbal shampoo formulations.

Evaluation Parameters of Herbal Powder Shampoos	
Organoleptic Evaluation	Color Odor Taste Texture Particle Size
General Powder Characters	Angle of Repose Bulk Density Tapped Density Packaging Criteria
Physicochemical Parameters (Evaluation)	Ash value Total ash Acid insoluble ash Moisture content pH
Cleaning action Foaming index (capacity) Dirt dispersion Wetting time Solubility Loss on drying Swelling index Nature of hair after wash	
Evaluation Parameters of Commercial Shampoos	
Physical appearance/visual inspection Determination of pH Determination % of solids contents Surface tension measurements Rheological evaluation Dirt dispersion Cleaning action Detergency ability Wetting time Foaming ability and foam stability Conditioning performance Stability study Eye irritation test Skin sensitization test	Clarity

3.2.2. Solid Shampoos

As mentioned before, the consumers' demand, related to a rapid hair and scalp cleansing, with additional benefits for hair softness and shine, is increasing the interest for the development of new shampoo formulations as, for example, the solid one. However, the innovations regard not only the product form (solid), but also the packaging and the use of novel interesting ingredients. These ingredients range from clays (mainly the Rhassoul clay) to herbs (Sheekakai, Reetha), as alternative washing bases, being already used as natural remedies in Moroccan and Indian traditions, up to washing flours (the most commonly used are chickpeas, millet, oats, rice starch or corn) [6].

Solid shampoos present some additional advantages compared to the traditional ones. In particular, they are easy to transport and can be used for a longer time, thanks to more microbiological stability than liquid formulations. Indeed, among ingredients, water is largely present in liquid shampoos and, for that reason, the use of preservatives is necessary. Solid shampoos, instead, could decrease or even eliminate water in the formula, thus reducing also the preservatives amount. Some cosmetic industries have already done this, especially in order to preserve water as a primary human resource, with respect to the eco-sustainability idea of a new era of cosmetic products. Among the first attempts to formulate a solid shampoo, some patents describe both the formulation of a solid bar shampoos and of dry shampoos. The first ones are based on SDS, as main anionic surfactant (from 70 to 90%), vegetable oils, preservatives, dyes, conditioning agents, perfumes and binding agents (as consistency factors), while the latter formulations presented are based on baking soda and corn starch [7]. In detail, it provides a dry shampoo composition comprising from 4 to 35% of baking soda and from 65 to 96% of starch. The product is proposed for a quick cleansing of children's hair, when wet washing is not desirable, and for sensitive and/or young skin with a sensitive scalp, avoiding frequent hair washes [23].

Clay Minerals as Natural Ingredients

Interestingly, the study of Carretero et al. [24] reports that clay minerals can be powerful in cosmetic products and especially for hair care, due to their peculiar properties. An overview about the use of clay in skin and hair care cosmetics is reported in the following, presenting also a general introduction regarding these minerals, and its wide-ranging potential application in the biomedical field, which could be useful for formulating novel solid shampoo formulations.

General Uses of Clays

For years, clay minerals were used for their beneficial effects on human health as active agents or excipients in many pharmaceutical preparations, utilized in different contexts [24]. In particular, as active agents, clays can be orally administered (for example in gastrointestinal protectors, osmotic oral laxatives, and antidiarrheals) or topically applied (dermatological protectors). As excipients, clays can be considered as a multitasking system, being lubricants, carriers, inert bases, viscosizing agents, stabilizing for suspensions and emulsions, as protection against environmental agents, for adhesion on skin and as grease adsorption agents, also as heat release controllers, and so on [25]. Interestingly, clays are also used in synergy with other rheological modifiers for influencing the stability and/or other properties of health care products [25].

Furthermore, among minerals used in pharmaceutical formulations that can be classified in different groups, i.e., oxides (for example rutile), carbonates (such as calcite, magnesite, etc.), sulphates, chlorides, hydroxides, elements (sulphur), sulphides (greenockite), phosphates (hydroxyapatite), nitrates, borates (as borax), there are phyllosilicates (smectite, palygorskite, sepiolite, kaolinite, talc, mica) [26]. Among the various important properties of these clay minerals, there are the high specific surface areas, great sorption capacity, favorable rheological characteristics, chemical inertness, and low or null toxicity, with the further advantage of lower price [24]. However, although the use of these natural minerals could be considered safe and rich with positive properties, the presence of some

elements, even if in trace quantities, may pose a potential threat for the patient due to their natural origin [27].

Clay Minerals and Clays

There is some misunderstanding in literature regarding "clay minerals" and "clays". If the first ones are a mineralogical term referring to part of a family (the phyllosilicates) consisting of hydrated aluminosilicates containing considerable amounts of Mg, K, Ca, Na and Fe and less common ions such as Ti, Mn, or Li, the latter word "clays" is frequently used in the same sense and, sometimes, it also refers to natural materials composed of very fine-grained minerals, with some plasticity when mixed with water and hardening on drying [28]. Clay minerals and clays are used in Pharmaceutical Technology and Dermopharmacy as excipients and as substances with interesting biological activity in solid (tablets, capsules and powders), liquid (suspensions, emulsions) or semisolid (ointments, creams) formulations [28]. Overall, in nature, it is possible to find clays of different colors: red, green, yellow, purple, blue, white, depending on the presence of iron and its chemical state. For example, if it is bivalent iron, the clays have a green color, while, if it is trivalent iron, the color turns to red; when the clay is white instead, it does not contain iron [15].

Chemical Composition and Impurities

The chemical composition of the natural clays used both in pharmacy and cosmetics is variable and it is mainly associated to the geological origin and to the associated minority minerals' content, not always easily detectable. Trace elements detected in these clays are also variable. For example, if elements as As, Sb, Cd, Co, Cu, Pb, Ni, Zn, Hg, Se, Te, Tl, Ba, etc, are considered toxic, Li, Rb, Sr, Cr, Mo, V, Zr, Rare-earth element (REE), are, instead, less dangerous. These trace elements could be located inside clay minerals structure and/or adsorbed on the surface [28]. The work of Rosselli et al. is interesting [27], in which essential and toxic elements (Al, Si, P, S, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Sr, Ba, Cd, Ce, Nd, Pb, U, Th, and La) were determined by energy-dispersive polarized X-ray fluorescence spectrometry in 15 samples of clay materials for pharmaceutical and cosmetic use. The investigated samples were grouped according to their mineralogical composition determined by X-ray powder diffraction. Samples consisting of smectites showed the lowest content of K, Zn, La, Ce, Nd, Pb, Ti, and Th and highest quantity of Sr, Br, and U. The sample containing smectite and kaolinite displayed the lowest content of Ca, Fe, Mn, Cu, Ni, and Sr and the highest amount of Al, Si, Ba, Zn, As, La, Ce, Pb, and Th. Samples composed of illite demonstrated minimal amounts of Br and maximal content of K, Rb, Ti, and Fe. In all samples analyzed, Cd and Hg levels were below 2 mg/kg [27].

Clay Minerals in Cosmetic and Health Care

Minerals are mainly used in cosmetic products as masks, sunscreens, toothpastes, creams, powder and emulsions, bathroom salts and deodorants [26]. However, due to the growing success of natural remedies, their use for wider cosmetic purposes is recently increased [24]. In the following, a list of potential applications in this field is reported:

- Clay minerals can be topically applied as dermatological protectors or for cosmetic reasons [29]. Creams, powders, emulsions used as cosmetic products, applied on the external parts of the body, embellish, modify physical appearance, and/or preserve the physico-chemical skin conditions. For example, as reported by Carretero et al. [26], clays with a high sorption capacity are present in creams, powders, emulsions for giving opacity, removing shine, and covering physical skin imperfections. Moreover, the ability of adhering to skin forming a protective film makes these materials able to absorb the excess sebum. For this purpose, the phyllosilicates group (such as palygorskite and sepiolite, in liquid preparations, kaolinite, smectites, and talc) is considered the most suitable [26]. In the case of pharmaceutical applications as dermatological protectors, clays are generally used in the form of powders, creams and ointments to protect skin against external

agents, and also in the case of exudations and liquid excretions. The most commonly used clays are kaolinite, talc and smectites, due to their high absorbent power [26,29]. Indeed, these minerals are capable of forming a film by adhering to skin and protecting it against external physical or chemical agents [29]. By absorbing the skin's secretions, they also have a refreshing action, producing a large surface for the evaporation, together with a gentle antiseptic action thanks to a water-poor environment, unfavorable for the development of bacteria. In this context, fibrous minerals (palygorskite and sepiolite) were considered the most suitable materials, but since there are doubts existing concerning the possible carcinogenic effect of palygorskite, if inhaled, their use as a dermatological protector is not desirable [26]. However, some authors report that these minerals are neither toxic nor dangerous [29].

- As functional ingredients in hair care cosmetics and in skin care mask formulations, clay minerals are used due to their high absorbency level of substances such as greases, toxins, etc.) [29]. Therefore, they are recommended for treating cutaneous inflammatory processes, such as seborrhoeic dermatitis, psoriasis, chronic eczemas or acne [26,29]. In particular, in the case of hair care applications, the addition of sulfur-containing minerals in shampoo formulations is considered an effective remedy against dandruff and seborrhoea [26].
- Clays and clay minerals are potential candidates as natural UV-protection agents in sunscreen formulations through mechanisms of absorption or reflection of UV radiation. Hoang-Minh et al. [30] studied the protective role of kaolin, smectite, mixed-layer series-dominated clay and mica-dominated clay against ultraviolet (UV) radiation, in the range 250–400 nm, due to the bulk Fe_2O_3 content that lowers the UV-transmission level. Additionally, the UV-protection depends on the expandability of the clay or the combination of clay mineral with mixed ointment [30]. Besides the direct use of clays as sunscreen, clays and clay minerals being used as delivery systems in cosmetic products, in order to improve the stability of an organic sunscreen like PABA (p-amino benzoic acid, an UV-B absorber in the range 200–313 nm), these new systems also open a novel horizon in the use of clays in this field as a promising, good, efficient way to protect other chemical filters. Moreover, as reported by Perioli et al. [31], these formulations allow a very low sunscreen release avoiding the close contact between skin and filter preventing at least cutaneous reactions and allergy problems.
- A clear distinction must be made between "healing clays" and those we have identified as "antibacterial clays". The antiseptic and disinfectant activity of these minerals is mainly due to a high astringent capacity, largely dependent on their concentration. It is worth underlining that high concentrations of these materials can be considered highly toxic to organisms. For this reason, their continuous application over large skin areas or over non-intact skin should be avoided [26]. While clays may heal various illnesses by means of their unique physical properties (e.g., high absorbance, high surface area, high heat capacity, high exchange capacity, etc.), only a few natural clays that kill pathogenic bacteria are reported. For example, among the healing clays, the researcher's attention was drawn to a clinical use of French green clay (rich in Fe-smectite) for healing Buruli ulcers, a necrotizing fasciitis caused by *Mycobacterium ulcers* [32]. On the other hand, white, gray and yellow clays have an antibacterial effect against *Staphylococcus aureus* (bacterial viability, colony-forming unit, CFU, of around 0 after 24 h) but have no effect against *Pseudomonas aeruginosa* exhibiting bacterial viability CFU from 80 to 100. Instead, under the same condition, pink clay explained an antibacterial effect against *Pseudomonas aeruginosa* (bacterial viability CFU of around 0) and has a low effect against *Staphylococcus aureus* exhibiting bacterial viability CFU of around 40 [33]. In spite of the use of geological mineral clay to heal skin bacterial infections having been evident since ancient times [33], the antibacterial process displayed by the identified clays is not yet well known [32]. Therefore, studies should be the focus in this direction since we are in the era of bacteria developing antibiotic resistance to existing pharmacological agents, and the discovery of new antibacterial agents, such as natural clay minerals, against pathogenic bacteria, could bring peculiar and great advantages [32]. For example, Williams et al. [32] reported that, under their conditions, the complete killing of *E. coli*, *S. typhimurium*, *P. aeruginosa*, and *M. marinum*

by the investigated clays was observed. Thus, their use could provide an inexpensive treatment for skin infections, especially in areas with limited access to hospitals and medical resources [32].

Clay Minerals Safety Specifications

About the use of these natural products, Pharmacopoeias and regulations report important information [28], devoted to different safety aspects associated with their processing, handling and administration. Since clay properties are also related to their colloidal size and crystalline structure, to a high specific surface area, to optimum rheological characteristics and/or to excellent sorption ability [28], their use depends on both structure and chemical composition. Overall, both as active ingredients or excipients, these minerals must conform with textural and compositional requirements, i.e., grain size, degree of mineral purity, water content, trace elements and microbial contamination, and appropriate technical properties [28]. It is worth mentioning that the material safety data sheets include relevant information established by the European Commission [28], including the identification of the substance, its principal intended or recommended uses, the composition/information on ingredients, hazards identification, handling and storage, physical and chemical properties, stability and reactivity, toxicological information, and a concentration range allowed in cosmetic formulations [28]. Although clays are considered by consumers as a non-toxic and a non-irritant when applied topically in low concentrations, it is important to recognize that cosmetic firms must verify the safety of their products [28,32]. Safety must also be guaranteed in terms of preservation of clays not only before the use, but also during the preparation of a cosmetic product; indeed, the use of metal containers should be avoided during the preparation and conservation of product containing clays.

Toxicological Evaluation of Clays

López-Galindo et al. [25] described some safety considerations about the use of clays starting from the consideration that clays used in pharmacology (treatment) or cosmetics (care and beauty) are usually taken as one, although their application field should be specified because it determines both technical aspects of their preparation as well as questions regarding code of practice and legal matters [28]. In particular, the Cosmetic Ingredient Review Expert Panel evaluation reported the safety assessment of the most commonly used clays, focusing also on their biological effects, being specifically interested in studies about clays adsorption, absorption, distribution, metabolism and excretion, and in-vitro assays [28]. The detailed review also commented on the results obtained from the experiments for testing acute toxicity, short-term and sub-chronic oral and parenteral toxicity in animals, inhalation toxicity, different types of irritation on skin, eyes and mucous membrane and the genotoxicity and carcinogenicity of such products [28]. Despite the inhalation toxicity being reported for animals (with particular attention to granulometry, particle shape, concentration and mineral composition, showing the greatest effect), since most of the formulations are not respirable and the clay concentration is very low, the analysis concluded that the available data were enough to evaluate clay safety used in cosmetic products [28]. As these substances vary widely in composition, texture and crystallinity, with significant effects on their properties, some of the tests, included in the main Pharmacopoeias, may be obsolete or imprecise since they are usually qualitative or semi-quantitative. Moreover, other properties, such as specific surface area or ion exchange capacity, determine the suitability of phyllosilicates, but are rarely taken into account [28]. About the toxicological data, additional information are also reported in literature [34]. For example, Tokarský et al. [34] describe the adsorbing properties of clays regarding heavy metals and organic compounds (pollutants and dyes) from water or soil. Thus, this could justify the reason why the clays should not be stored or handled in metal containers. About this aspect, some authors, in their study, determined the presence of heavy metals such as Lead, Cadmium and Copper inside samples of clays from different origin. Results are important to guarantee the safety of cosmetic products as well as the quality and effectiveness [35].

Clays Tests

For pharmaceutical or cosmetic applications, clays must fulfil various chemical (stability, purity, chemical inertia), physical (texture, water content, particle size) and toxicological (toxicity, safety and microbiological purity) requirements. Therefore, the Pharmacopeias recommend different tests because their usage for a specific application is dependent on its chemical and mineralogical composition (for example the type of clay mineral) and on its mineral structure (1:1 or 2:1 layer type) [36]. Indeed, the technical behavior of a clay could change due to the presence different mineral phases determined by different cations in the octahedral sheet, or by isomorphic substitutions in the octahedral and tetrahedral sheets [36]. Regarding this aspect, Desideri et al. [36] used the examples of kaolinite and talc, which present low cation-exchange capacities, due to the reduced layer charges. Instead, the smectites are characterized by high ion-exchange capacities thanks to octahedral and tetrahedral substitutions. The most significant tests are related to identification of clay minerals, pH, microbial limit, water content, quantity of acid soluble substances, and the presence of impurities as trace elements, since the presence of some elements may pose a potential risk for the user [27]. However, differently from the herbal shampoos, there are no descriptions in the literature about the evaluation parameters of clay and clay minerals in solid shampoo formulations. To guarantee greater consumer safety, as well as the quality and effectiveness of these products, it would be important to implement the academic studies in the evaluation of these parameters, also by comparing it with herbal shampoos.

Clays' Cleaning Properties

As already said, clays are versatile ingredients in cosmetic field due to their many properties, including the detergent one. In fact, some clays, if wet with water, behave like detergents and so, they were usually used for hand and body hygiene well before the introduction of soaps, on the industrial-scale [15]. Indeed, these substances, through an adsorption process due to the ability of the particles that compose them to attract and fix some greases on their surface, are able to remove impurities. In particular, this process occurs also at a cutaneous level when clays, after being applied in gel form, subtract fats and impurities [15]. Accordingly, in recent times, hair care cosmetic formulation technologies have focused the attention on washing clays, among which the use of Rhassoul clay in shampoos is highlighted, together with washing herbs. With regard to this, there are various patents (see, for example, [37]), in which authors report solid shampoo formulation using Rhassoul clay, glycerin and natural extracts as conditioning agents [37]. In particular, the Williams' invention relates to compositions for a multi-benefit hair care product, acting as a shampoo or a cleanser, as smoothing conditioner, as deep conditioner and as a leave-in conditioner.

Rhassoul Clay

The Rhassoul clay is an outstanding naturally found reddish-brown clay that originates from Morocco, traditionally used in skin and hair care formulations as soap, shampoo and conditioner [8,38]. It is also known by the names Red Clay, Red Moroccan Clay, Ghassoul Clay and Oxide Clay [38]. Its etymology derives from the Arabic verb Rhassala which means 'to wash' [38]. Not surprisingly, due to its diffused use, the official Moroccan Pharmacopoeia reports specifications and uses of Rhassoul [38]. Due to its good detergent property, Rhassoul clay can be used as a washing base in several shampoo formulations (especially against oily hair), but, thanks to its simplicity of use, it is often also used as a mask in hair treatments [8]. Moreover, Rhassoul, containing natural minerals that act as natural detoxifying and nourishing, is also used in several skin care products, from masks to anti-acne creams, as a principal ingredient [8]. However, it is worth mentioning that the natural Rhassoul clay is characterized by a basic pH, so, when employed in a shampoo formulation, the use of a pH neutralizer for reaching a pH value that is suitable for hair and scalp physiology is necessary [37]. The Rhassoul clay composition, related to the nature of the pure mineral clay fraction which is claimed stevensite (belonging to the smectite group), is controversial. Overall, the XRD data revealed that the raw

Rhassoul clay consists mainly of a Mg-rich trioctahedral smectite, with the presence of impurities such as quartz and dolomite [35,38]. Rhouta et al. [39] reported that the mineral fraction of the clay contains also a larger amount of Al (>1 wt.%) if compared with other stevensite. The Moroccan official bulletin (No. 3202; March 1974) defined Rhassoul clay as a product made up of 90% of stevensite and Al_2O_3 that could reach 5 wt.% [39]. According to the first article of the Moroccan Decree n° 2-73-370, dated 5 March 1974, the products can only be marketed under the name 'Rhassoul', if they contain at least 90% w/w of the clay mineral known as stevensite and Li (Hectorite) [38].

4. Conclusions

Shiny hair having a smooth texture and clean-cut ends is generally perceived to be healthy. In recent years, the consumers' demand of product for hair care is increased, especially in the field of natural products. Thus, this review focuses on hair care and technologies known in the cosmetics, highlighting the importance of shampoo in different form and formulations. Information about traditional shampoo, herbal shampoo and solid shampoo are reported. Since there is information available about the liquid and herbal shampoo, more information about the solid shampoo is reported, focusing the attention, among ingredients, on natural clays. Indeed, the general use of natural ingredients is strengthened during the review, bringing out the importance of clay in solid shampoo formulations. An overview about the clay importance is reported describing the properties and advantages of this mineral ingredient. Solid shampoo as a multitasking product for consumers looking for hair care cosmetics that are ecofriendly and effective in cleansing is described well. Specifically, this cleansing must be "mild", in order to respect the physiology of hair and scalp, leaving a feeling of softness and shine on the hair in order to maintain its well-being. However, this does not mean that clay-based solid shampoos, i.e., containing, for example, Rhassoul clay, are better than other shampoos formulated with washing herbs or washing flours, but, they should rather be considered as an alternative to traditional products, exhibiting several advantages. Indeed, the challenge of cosmetic technology is to develop new strategies and techniques for the formulation of cosmetic products consisting mainly of natural origin ingredients, lowering the associate costs, and meeting the consumer requests.

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