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Cleaner Processes for Making Laundry Soap from Vegetable Oils and an Essential Oil

Valentina-Gabi Stănescu [1], Vasilica Popescu [1,*], Viorica Vasilache [2], Gabriel Popescu [3,*], Cristina Mihaela Rîmbu [4] and Andrei Popescu [3]

[1] Department of Chemical Engineering in Textiles and Leather, Faculty of Industrial Design and Business Management, "Gheorghe Asachi" Technical University of Iasi, 700050 Iași, Romania; sandragabi1967@yahoo.com
[2] Laboratory of Scientific Investigation and Cultural Heritage Conservation, "Alexandru Ioan Cuza" University of Iași, 700506 Iași, Romania; viorica_18v@yahoo.com
[3] Department of Machine Design, Mechatronics and Robotics, Faculty of Mechanical Engineering, "Gheorghe Asachi" Technical University of Iasi, 700050 Iași, Romania; andrei.popescu@academic.tuiasi.ro
[4] Department of Public Health, "Ion Ionescu de la Brad" University of Life Sciences of Iași, 700490 Iași, Romania; crimbu@yahoo.com
* Correspondence: vasilica.popescu@academic.tuiasi.ro (V.P.); gabriel.popescu@academic.tuiasi.ro (G.P.)

Abstract: This article demonstrates that the quality of laundry soap obtained by hot/cold saponification of two vegetable oils (olive and coconut) and an essential oil (such as Neem, Tea Tree or Thyme) influences the effects obtained after washing textiles: cleansing capacity and antibacterial effect. The results of FTIR, SEM, EDX, thermogravimetry and colorimetry analyses are presented comparatively for hot- and cold-prepared soaps. Saponification, Iodine number and Iodine Number Saponification values are determined for each oil but also for the mixture used in soap-making. Soap quality refers to texture, hardness, foaming capacity, stability, durability, cleansing capacity after washing and antimicrobial capacity. The removal power of greasy dirt (heavy used engine oil) of these laundry soaps is higher than that of some commercial soaps, obtaining dirt visibility <2.6% after washing at 100 °C, soiling addition density SAD < 0.0229 and cleansing capacity between 80.88 and 92.16%. UV-VIS analysis confirms the presence of essential oil in soaps (even after 10 months from manufacture) but also in textiles washed with them. The essential oil imparts strong antimicrobial properties to the laundry soaps (since they do not allow for attachment or multiplication of microorganisms from the environment), which makes them particularly useful in washing and disinfecting textile products used in hospitals.

Keywords: Neem; Tea Tree; Thyme; saponification; dirt visibility after washing; soiling addition density; cleansing capacity; antimicrobial effects

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1. Introduction

For household laundry, the use of detergents is preferred. Laundry detergents are obtained by mixing several ingredients: surfactants (with synthetic origin), builders (to extend the cleaning performance), and multiple additives (bleaches, bleach activators, softeners, enzymes, scouring agents, fabric brighteners, anticaking agents, thickening agents, pearlescent agents and opacifying agents) [1].

Detergents have a high capacity to remove dirt from laundry but they heavily pollute wastewater, which is why it is necessary to find a solution to eliminate this inconvenience [2,3]. The components used in the manufacture of detergents affect flora and fauna through both direct and indirect effects on ecosystems. The presence of

phosphate salts (between 35% and 75%) in the composition of some detergents causes a variety of water pollution problems because phosphates tend to inhibit the biodegradation of organic substances or can contribute to water pollution by promoting excessive algae growth, which can lead to oxygen depletion in the water, and, consequently, the survival of marine life becomes impossible [4–6].

In order to reduce wastewater pollution, since 2004, the European Union countries, with the support of environmentalists, have developed a regulation (Regulation (EC) No. 648/2004 of the European Parliament and of the Council) to limit the phosphate content of a laundry detergent [7]. Another option would be to replace synthetic detergents with natural cleaning products, which are more sustainable and environmentally friendly due to the biodegradable nature of the ingredients in their composition [8–10].

Therefore, replacing synthetic detergents with natural cleaning products would be beneficial [8,9]. A natural cleaning product is one made only from natural ingredients, without synthetic or artificial ingredients [11]. Natural soap is made from ingredients originating from fruit/plants in nature, while detergents are manufactured from synthetic sources (petroleum fractions). Generally, a detergent contains a surfactant, chelators, dispersing agent, stabilizers and perfume, which cause the wastewater to be loaded with non-ecological products, some of which are non-biodegradable [12].

The design of a laundry soap formulation recipe should take into account the participation in the saponification process of a small number of non-polluting chemicals, such as vegetable oils or animal fats, and an alkali such as NaOH [13,14]. It is known that, during saponification, a hydrolysis reaction occurs due to the nucleophilic attack of the hydroxyl ion (from alkalis) on the C=O group in the ester bonds existing in the triglyceride molecule. As a result, these ester bonds break (between glycerol and the three fatty acids linked to it), resulting in fatty acid salts (soaps) and glycerin [15]. A similar hydrolysis reaction occurs if enzymes (such as lipases) are used under certain conditions (lower temperatures and neutral pH); so, enzymatic hydrolysis can be considered an alternative to conventional saponification [16–18]. To further minimize the environmental impact or improve the efficiency of soap, eco-friendly alternatives can be used that target both the substances used in saponification (sustainable, biodegradable, natural, ethically sourced and plant-based fats/oils and additives) and the processing techniques (more energy-efficient, such as cold processing or in microreactors equipped accordingly to minimize water consumption and waste generation).

Non-irritating, non-polluting soaps can be obtained through cleaner saponification processes in which the use of auxiliaries and additives (compounds containing Fe, Cu, Zn, Cr, and Mn ions, borax, ethyl alcohol, stearic acid, pigments, etc.) is avoided [19,20]. The ions mentioned should be avoided in soap formulation because they can generate insoluble soaps, ineffective for washing [21]. The nature of the metal ion influences the solubility and stability of the soap in solutions. Their presence in wastewater will make the purification process more difficult. In addition, avoiding other synthetic chemicals in soap manufacturing is necessary to maintain the syntagma of *natural soap*, i.e., formulated only with ingredients from nature.

The success of natural soaps depends on factors such as raw material quality, final product quality, marketing strategy, and customer satisfaction. Comparing the life cycles of soaps with those of detergents, it is found that natural soaps have a lower impact on the environment in each of the five stages, as follows:

- *In the case of natural soaps:* (1) raw materials: renewable plant-based oils, biodegradable ingredients; (2) production: simpler, low energy consumption, minimal waste generation; (3) packaging: paper, cardboard, and therefore biodegradable packaging; (4) use:

biodegradable product, minimal environmental impact, low water consumption; (5) end of life: biodegradable, minimal waste if the packaging is ecological [22].

- *In the case of detergents:* (1) raw materials: non-renewable chemicals, petroleum-based, high carbon footprint; (2) production: more complex, energy-consuming, generates chemical waste; (3) packaging: non-ecological packaging, in plastic bags that lead to significant waste generation; (4) use: pollute water, contain non-biodegradable compounds, high water consumption; (5) end of life: plastic waste, non-biodegradable chemicals persist in water systems [23–29].

The raw materials used to obtain a natural soap refer to triglycerides in the form of vegetable oils or animal fats that contain saturated and unsaturated fatty acids, with long alkyl chains and which, during the saponification process, are transformed into soaps [30].

Although both saponification variants use the same ingredients (triglycerides and alkali), there are differences in temperature and time during the saponification process.

In the presence of a strong alkali, the reaction can easily take place hot (1 h), or cold (after a minimum of 1 month of ripening). When saponification is carried out hot, there is a single stage of making the soap, which can be used immediately after the cooling stage. The cold saponification process takes place in two stages: the first stage consists of starting the cold saponification by mixing the oils, fats with NaOH, and, in the second stage, ripening takes place, that is, the slow development of the saponification reaction, for 1 month when exposed to a well-ventilated and moisture-free environment [31,32]. These storage conditions are necessary to prevent any moisture build-up that could affect the soap; it is established that, during the maturation stage, soap undergoes a slow evaporation process, in which excess water is removed, thus allowing the soap to harden properly. It is also necessary to regularly monitor environmental conditions, such as temperature, humidity and exposure to light, as fluctuations in these conditions can negatively affect the quality of the soap, leading to problems such as melting, discoloration or the development of rancidity [33–38].

The two types of saponification processes lead to the formation of glycerin and a mixture of fatty acid salts. These carboxylate salts are actually mixtures of soaps [39,40].

When soap is formulated at home, the final product has better qualities for both human skin and washed laundry. If glycerin formed as a by-product of the reaction is not removed for use in other areas, it functions as an emollient for hand skin and as a good antistatic/softening agent for laundry washed with such soaps [39,41].

Soaps, like laundry detergents, have a high cleaning capacity because they contain two parts: a polar part (carboxylic group), with an affinity for water, and a nonpolar part (hydrocarbon chain) with an affinity for greasy dirt [42].

Another component that can be added at the end of saponification to give natural soap a fragrant scent is actually an essential oil. This is chosen not only for the smell but also for the additional effects it offers to the soap.

Essential oils are extracted from plants such as *Azadirachta indica A. Juss* (Neem), *Melaleuca alternifolia* (Tea Tree) and *Thymus vulgaris* L. (Thyme). The Neem essential oil can be used because it has multiple effects: anti-irritant, antimicrobial, antiseptic, insect repellent, purifying, and antifungal [43–46].

The composition of *Neem essential oil* depends on the raw material used in the extraction process (seeds, leaves or fresh flowers) of the *Azadirachta indica A.* Juss plant. Other factors are related to the geographical area in which the plant is grown, namely, the climate and nutrients in the soil. Thus, Neem essential oil extracted from the seeds of the plant cultivated in Iran has as main components several fatty acids (about 53.5%) (such as hexadecanoic acid (34.0%), oleic acid (15.7%), methyl oleate (3.8%)) and aroma-active

compounds (5,6-dihydro-2,4,6-triethyl-(4H)-1,3,5-dithiazine (11.7%), and a sesquiterpene (eudesm-7(11)-en-4-ol (2.7%)) [47,48].

Neem essential oil extracted from *fresh Neem flowers* (from Iran) obtained by steam distillation contains sesquiterpenes, aromatic compounds, fatty acids, fatty acid esters, steroids, hydrocarbons δ-cadinene (9.43%) α-copaene (7.03%), humulene (3.7%), δ-cubebene (3.04%), some sesquiterpenes, and unidentified organo-sulfur compounds [49–51].

Neem essential oil extracted from *Neem Leaves* (from Iran) contains, in addition to the seeds or flowers, the compounds γ-elemene (20.8%), germacrene-B (20.3%), trans-caryophyllene (13.5%), hexadecanal (12.8%), and methyl linoleate (10.5%).

Neem essential oil extracted from the leaves of the plant cultivated in India has the following components, identified by ^{1}HNMR analysis: azadirachtin I, azadirachtin A, deacetylnimbin, deacetylalannin, deacetyl nimbin, salannin, nimbin, quercetin-3-rutinoside, quercetin and kaempherol (as natural flavonoids) [52,53].

Another study indicates that the essential oil extracted from Neem seeds collected in Senegal is mainly composed of non-terpene compounds with sulfur and nitrogen (about 80.2%) and few terpene compounds, mainly sesquiterpenes (about 7.5%) [54].

Neem essential oil, in smaller proportions, contains n-alkanes, aromatics esters, sulfur and nitrogen compounds and terpenoids [48–53]. The volatile components of Neem essential oil are cis- and trans-3,5-diethyl-1,2,4-trithiolanes [49].

This variability in composition could influence the effectiveness of Neem essential oil in different applications, including soap formulation.

The composition of Neem essential oil is particularly complex because it contains a large number of different phytochemicals, such as terpenes (monoterpenes, sesquiterpenes, diterpenes, sesterpenes, and triterpenes) and terpenoids. The composition of terpenes and terpenoids, their chemical structures, and the effects produced by them are presented in the literature [55].

Knowing the percentages of terpenoids in Neem essential oil is important because they influence the intensity of antibacterial and antifungal effects. So, according to the literature, the components responsible for the antimicrobial effects are diterpenoids (sugiol, nimbosone, nimbilicin, margosone and its derivatives), cyclicditerpenoids (margosolone, nimbinol, nimbionol, nimbionone, nimbisonol, nimbisodione, nimbosone, nimosone, methyl nimbiol, methyl nimbionone, isonimbinolide, dimethyl nimbionol, sugiol), triterpenoids (nimocinol, Azadirahemiacetal), tetranortriterpenoids (nimbidic acid, nimbidinin), tetracyclictriterpenoid (nimocinol), and sesquiterpenoids (β-farnesene) [56].

Tea Tree essential oil extracted from *M. alternifolia* leaves contains α-pinene (21.64%), φ-terpinene (21.09%), terpinen-4-ol (17.31%), limonene (9.37%), and o-cymene (6.54%). The literature presents the composition of Australian Tea Tree essential oil according to gas chromatographic analysis: 93.6% terpene hydrocarbons (as Terpinen-4-ol (40.1%), γ-Terpinene (23%), α-Terpinene (10.4%), 1,8-Cineole (5.1%), Terpinolene (3.1%), ρ-Cymene (2.9%), α-Pinene (2.6%), α-Terpineol (2.4%), Aromadendrene (1.5%), δ-Cadinene (1.3%), Limonene (1%), Sabinene (0.2%)) and 0.3% related alcohols (Globulol (0.2%), and Viridiflorol (0.1%)) [57,58].

The main chemical constituents of Tea Tree essential oil obtained by steam distillation from the fresh leaves and twigs of *Melaleuca alternifolia* plants grown in South Africa are 1-terpinen-4-ol (at least 30%), 1,6-cineole (less than 15%), pinene, terpinenes, carmine, sesquiterpenes, and sesquiterpene alcohol.

The essential oil of Thyme (*Thymus vulgaris* L.) contains five classes of compounds: monoterpene hydrocarbons, oxygenated monoterpene, sesquiterpene hydrocarbons, oxygenated sesquiterpenes and others.

Its main constituents are alpha-thujone, alpha-pinene, camphene, beta-pinene, para cymene, alpha terpinene, linalool, borneol, beta-caryophyllene, thymol, and carvacrol. The predominant compound of this essential oil composition is thymol (51.34%), while the amount of all other components of the oil (as γ-terpinene, p-cymene, carvacrol, and linalool) is found to be lower than 19% [59,60].

Thymol, being predominant, determines the greatest antimicrobial effect and the other components confer both a synergistic effect and anti-inflammatory properties [61].

During saponification, temperature can affect the properties of the essential oil or raw material (fats/oils), which will be reflected in the final quality of the soap [39,62], as follows:

1. In the case of cold saponification, very-good-quality soaps are obtained, with a smooth surface and a well-defined geometric shape, which preserve the nutrients in the raw material, retain the additives better, as well as the glycerin.
2. In the case of hot saponification, good-quality soaps are obtained but are harder, slightly shiny, with a less fine appearance and a rougher texture because they contain fewer nutrients and glycerin due to its thermal degradation during processing.

The efficiency of saponification can be appreciated according to the speed/production time or according to the energy consumption. From these points of view, cold saponification requires a longer production time (due to the maturation time of at least 4 weeks) but requires minimal energy consumption. Hot saponification generates soaps that can be used 1–2 days after production, but the energy consumption required to obtain these soaps is high.

In both saponification processes (hot/cold), glycerin is also a result of the reaction by-product, which, not being removed, gives laundry soap the ability to improve the feel of washed laundry (as a fabric softener) and reduce electrostatic charge in textiles.

The novelty of this article lies in the design of three natural laundry soaps, through cleaner saponification processes, obtaining exceptional washing and antimicrobial capacities. The cold/hot saponification processes based on two vegetable oils (olive and coconut) and an essential oil (Neem, Tea Tree and Thyme), considered safe by GRAS (Generally Recognized as Safe), generate soaps that do not cause any irritation or allergies and do not pollute wastewater and implicitly the environment. The influence of the essential oil on the effects created on textile materials, after washing with these soaps, is analyzed.

The characteristics of these laundry soaps (pH, foaming, cleaning capacity, color) are superior to those of the commercial soaps used for comparison.

This is the first time that the washing/cleaning capacity of soaps is quantitatively assessed by measuring the L*, a*, b* values on a high-precision Data Color spectrophotometer. The results of the colorimetric measurements are used to calculate three quantities indicating the absence of used engine oil stains after washing with these soaps:

1. Hidden stain visibility after washing (Hs);
2. Soiling Additional Density (SAD);
3. Percentage cleanability (PC).

The presence of essential oil remaining in the washed laundry is evidenced by UV-VIS analysis. The antimicrobial capacity is quantitatively evaluated by determining the total number of germs/products produced after 48 h and is due to residual essential oils.

The formula for each new-formulated soap is the result of a long series of experiments. Manufactured using cleaner processes, without additives, these soaps have a greater cleaning power than many detergents or soaps on the market.

2. Materials and Methods

The laundry soaps are prepared from a mixture of 2 vegetable oils: olive pomace oil (INCI: Olea Europaea (Fruit) Oil) and coconut oil (INCI: cocos nucifera (coconut) oil). For comparison, the soaps are also manufactured from a single type of vegetable oil (olive pomace and coconut oil) by hot and cold processes.

The vegetable oils were purchased from the company Dried Fruits (Bucharest, Romania). They were obtained in 2024 and have a 2-year shelf life.

Neem (*Azadirachta indica*), Tea Tree (*Melaleuca alternifolia*) and Thyme (*Thymus vulgaris* L.) are used as essential oils.

To characterize the oils used in the saponification process, the substances alcoholic KOH, HCl, phenolphthalein, CCl_4, Iodine/KI, $Na_2S_2O_3$ and soluble starch are used. For the comparative analysis of the formulated soaps, 2 laundry soaps (Popular (Sidoarjo, Indonesia) and ChanteClair (Seregno, Italy)) sold in Romania and 3 detergents such as Fairy (Procter & Gamble, Cincinnati, OH, USA) (specially for removing grease), a Reference detergent ICE Non-Phosphate (A) incorporating an optical brightener (abbreviation DA) and a Reference detergent (B), ECE phosphate, without optical brightening agent (DB), are used. The selection of the 2 laundry soaps for comparison is based on both their widespread use in Romania and their cleaning capacity. In the case of ChanteClair soap, another criterion is the similarity in formulation because it is obtained by saponifying olive oil, a vegetable oil that also predominates in the new laundry soaps formulated and tested in this article.

The choice of the 3 detergents is based on their well-known ability to remove greasy impurities. In addition, the two detergents abbreviated as DA and DB are reference detergents and are commonly used in oily soil removal tests. However, since the used engine oil stain is very pronounced, the tests are carried out both at 60 °C (according to AATCC Test Method 130–2000) and at higher temperatures (95 °C and 100 °C) for good comparisons. It is known that the choice of washing temperature depends on the degree of soiling, the depth of the stains, and the nature of the soiled fabric.

2.1. Experimental Protocol

The choice of saponification method for soap formulation takes into account the properties, the time required to obtain the soap, and the destination (toilet or laundry). For a less harsh soap, which will retain its scent for a long period of time, cold saponification is preferable because the low temperature does not accelerate the volatilization of some compounds from the essential oils included in the soap. In contrast, harder soaps, made faster, can be formulated by hot saponification. By practicing cold (30 °C, 30 min with continuous stirring) and hot saponification (100 °C, 1 h with continuous stirring), several ecological soaps are formulated using olive pomace oil (50 g), coconut oil 76 degrees (21 g) and an essential oil: Neem or Tea tree (ratio 31), or Thyme (ratio 16.9). In soap formulation, the perfume ratio (31 and 16.9) refers to the mass of essential oil added to 1000 g of the base oil mixture (olive and coconut). In Table 1, the essential oil concentration in the saponification recipe, expressed as a percentage, actually refers to the mass of essential oil added to 100 g of base oil mixture. Throughout the saponification process, strong and continuous stirring is practiced. The addition of the essential oil is carried out at the end of the saponification process and to obtain good homogeneity of the mixture of saponified oils, mixing is continued for another 5 min. The recipes used to obtain the soaps are shown in Table 1.

Table 1. Experimental protocol for the manufacture of natural soaps.

Saponification Method	Soap Code	Saponification Recipe			
		Oil Name	Oil Percent (%)	Essential Oil Name	Weight of Essential Oil (%) (g/100 g Base Oil Mixture)
Cold saponification	CS1	Olive pomace oil Coconut oil 76 degrees	70.42 29.58	-	-
	CS2	Olive pomace oil Coconut oil 76 degrees	70.42 29.58	Neem	3.1
	CS3	Olive pomace oil Coconut oil 76 degrees	70.42 29.58	Tea Tree	3.1
	CS4	Olive pomace oil Coconut oil 76 degrees	70.42 29.58	Thyme	1.69
	CM	Olive pomace oil	100	-	-
	CC	Coconut oil 76 degrees	100	-	-
Hot saponification	HS1	Olive pomace oil Coconut oil 76 degrees	70.42 29.58	-	-
	HS2	Olive pomace oil Coconut oil 76 degrees	70.42 29.58	Neem	3.1
	HS3	Olive pomace oil Coconut oil 76 degrees	70.42 29.58	Tea Tree	3.1
	HS4	Olive pomace oil Coconut oil 76 degrees	70.42 29.58	Thyme	1.69
	HM	Olive pomace oil	100	-	-
	HC	Coconut oil 76 degrees	100	-	-

Other information regarding the formulated soap recipes: mass of the oil mixture for formulating a soap = 71 g; water as percent of oil weight = 38.00%; lye concentration = 28.112%; water: lye ratio = 2.5572:1; fragrance ratio =16.9–31 g/1000 g base oil mixture (olive and coconut). Super Fat/Discount = 0%; Super Fat/Discount of 0% is specific to the formulation of laundry soap meaning zero excess of fat/triglycerides in the recipe. This means that there are no additional oils left unreacted at the end of the soap-making process. With these recipes, the soaps will be drier, harder and less smooth on the skin, but have a very good cleansing effect.

Due to the strong fragrance of Thyme essential oil, only a percentage of 1.69 is used in the formulation of CS4 and HS4 soaps as a precautionary measure so that these soaps can also be used by people sensitive to odors, such as those with bronchial asthma.

The concentrations of Thyme essential oil (1.69%) and Neem (3.1%) could give the laundry soap mild and gentle antimicrobial capacities, a pleasant, non-irritating fragrance, and a certain cleaning power. In contrast, the concentration of 3.1% for Tea Tree essential

oil could induce strong antimicrobial and antifungal capacities, a good cleaning capacity, and a strong but pleasant fragrance.

2.2. Methods and Analyses

In this article, 4 types of analyses are performed to analyze the vegetable oils used in the soap formulation, to confirm the presence of essential oil in the soap, to determine the physical characteristics of the soap, and to indicate the quality and efficiency of the soap.

2.2.1. Analysis of Vegetable Oils Used in Soap Formulation

Determination of Saponification Value (SAP) of Oils

The SAP is determined according to the AOCS Method cd 3–25 standard [63]. SAP values are determined for both the 2 oils used in the saponification process (olive and coconut oil) and for a blank sample. For this purpose, 1 g of oil is added to an Erlenmeyer flask, where 25 mL of 1 N alcoholic KOH solution is added. A condenser container is attached to it and the assembly is placed in a water bath, where it is kept boiling for 1 h. After cooling, 0.5 mL of 1% alcoholic phenolphthalein is added to the solution resulting from saponification when a magenta color is obtained. Using a 0.5 N HCl solution, titrate until the magenta color disappears and the liquid becomes colorless.

The following mathematical Equation (1) is used to calculate the SAP value [64]:

$$SAP = [(V_B - V_S) \times N_{HCl} \times 56.1]/W \text{ [mg KOH/g oil]} \quad (1)$$

where $V_B = V_{\text{blank sample}}$; $V_S = V_{\text{sample}}$ = volume of 0.5 N HCl solution used in titration; N_{HCl} = normality of HCl solution; 56.1 = molecular weight of KOH used for saponification of oils (g); W = mass of oil sample (g);

SAP can also be expressed in (g KOH/1 g oil).

Iodine Number (IN)

The IN is a measure of the amount of unsaturated fatty acids present in the triglycerides/oils/fats used in the soap formulation. The IN value influences the final properties of the soap, such as its cleaning power, texture, stability and durability.

IN values give anticipatory indications on the final properties of the soap, as follows:

1. *Cleansing capacity*: when the IN value of the triglycerides is higher (as a measure of the unsaturation of the component fatty acids), the cleansing capacity of soap is higher; in this case, the soaps have a greater capacity to extract/displace and emulsify oils and dirt.
2. *Texture and hardness:* Low IN values often occur with saturated fats and indicate the attainment of harder and more solid soaps at room temperature. High IN values are specific to unsaturated fats and indicate the creation of softer soaps.
3. *Stability and durability:* high IN values indicate a risk of rancidity, which is caused by the oxidation of unsaturated fatty acids and can be accelerated by factors such as exposure to light, heat, and air; in this case, the soap has a shorter shelf life [65].

The saponification recipe is designed using a mixture of olive oil (with high IN) and coconut oil (with low IN) precisely to create a soap that has both moisturizing properties and a long-lasting, bubbly lather in a moderate amount, as is necessary for a laundry soap.

The IN is determined according to AOCS Method cd 1-25/1993 [63].

In an Erlenmeyer flask, over a quantity of 0.3 g of oil, 20 mL of CCl_4 and 25 mL of iodine/KI solution are added, with the mixture being shaken vigorously. This is followed by 30 min of incubation, in the dark, at room temperature. Then, 200 mL of distilled water is added to stop the reaction and then titrated with 0.1 N sodium thiosulfate solution.

The titration is completed when the yellow-violet color disappears. Then, 0.5 mL of a soluble starch solution, with a concentration of 1%, is added when the blue color appears. The titration is continued using the same 0.1 N sodium thiosulfate solution until the blue color disappears and the solution in the beaker becomes colorless [66].

The volume of sodium thiosulfate used in the titration is read on the burette.

The IN index is calculated with the mathematical Equation (2) [67]:

$$IN = [(V_B - V_S) \times N_{thiosulfate} \times 12.69]/W \text{ [mg iodine/g oil]} \quad (2)$$

where $V_B = V_{blank}$, for blank sample vs. $= V_{sample}$ = volume of 0.5 N sodium thiosulfate used in the titration; 0.1 = normality of the sodium thiosulfate solution; 126.9 = molecular weight of sodium thiosulfate (g); W = mass of the oil sample = 0.3 g.

The IN value can be converted to g iodine/100 g oil to express the number of grams of iodine absorbed by 100 g of oil.

Saponification Iodine Number (INS)

The INS is actually a way to quickly identify mixtures of triglycerides that saponify easily and give a hard soap.

The INS value describes the physical qualities of oil. The INS represents the difference between the SAP value and the IN index [31,67].

Analysis of the Mixture of Oils in Soap: SAP, IN and INS of Oil Mixture

For the mixture of the 2 vegetable oils, the values of the SAP, IN and INS can be determined according to the literature [31]. In this article, the calculations are performed according to Equations (3)–(5):

$$SAP_{oil\ mixture} = 70.42/100\ SAP_{olive\ oil} + 29.58/100\ SAP_{coconut\ oil} \quad (3)$$

$$IN_{oil\ mixture} = 70.42/100\ IN_{olive\ oil} + 29.58/100\ IN_{coconut\ oil} \text{ [g iodine/100 g oil]} \quad (4)$$

$$INS_{oil\ mixture} = SAP_{oil\ mixture} - I_{oil\ mixture} \quad (5)$$

The INS takes into account the saponification value of the oils, the SAP and the IN [67].

2.2.2. Analyses Confirming the Presence of Essential Oil in Soap

FTIR: Infrared spectroscopic analysis is performed on Bruker Optics equipment (Bruker Optik GmbH, Ettlingen, Germany), comprising a TENSOR 27 FTIR spectrophotometer (Bruker Optik GmbH, Ettlingen, Germany), coupled to a HYPERION Microscop 1000 (Bruker, Corporation, Billerica, MA, USA) equipped with a standard 15 objective.

SEM, EDX and Map: Several spectroscopic analyses are performed on a SEM microscope model VEGA II LSH (TESCANS.R.O., Brno, Czech Republic) coupled with a 3rd-generation EDX detector, model QUANTAX QX2 (BRUKER Optics, Ettlingen, Germany): SEM (Scanning Electron Microscopy), Map (elemental mapping) and EDX (Energy Dispersive X-ray).

UV-VIS: A Camspec M501 (Spectronic CamSpec Ltd., Leeds, UK) spectrophotometer is used to analyze the solution consisting of 0.1 g of soap dissolved in saline and distilled water. Cotton samples washed with cold or hot saponified soaps are maintained in saline and distilled water, or in ethanol to extract the residual essential oil. Absorbance is measured between 190 and 700 nm.

Thermal Analysis/Thermogravimetry TGA and DTA: A computer-assisted Linseis STA PT-1600 thermobalance (Linseis Messgeraete GmbH, Selb, Germany) with simultaneous recording of thermogravimetric curves is used for the thermal analysis of the soap sam-

ples. The heating rate is 10 °C/min in a dynamic air atmosphere and a gas flow rate of 50 mL/min, maximum temperature 400 °C; the soap samples weighed 50 mg, measured on a PARTNER AS220/C/2 electronic balance.

2.2.3. Analyses Indicating the Physical Characteristics of Soap

The *pH of the soap* is determined according to a slightly modified method presented in the literature [68]. A solution of 50 mL of distilled water and 1 g of soap is stirred until the soap is dissolved. The pH value is measured after 30 min.

Foaming capacity of the soap: In a 500 cm^3 graduated cylinder, 100 mL of a 1 g/L soap solution is added. The solution is shaken vigorously for 10 s and then allowed to stand for 10 min. The height of the foam in the graduated cylinder is noted.

*CIEL*a*b* color measurements* are performed on a Data Color spectrophotometer. Luminosity L*, red/green (a*) and yellow/blue (b*) hues are measured for each soap and for cotton samples soiled, and then washed with soap solutions. The accuracy of the color measurement analysis and reproducibility are ensured by the Root Mean Square of Color Difference method [69].

The steps performed consisted of the following:

1. For each analyzed sample, the color is measured (as L*, a* and b*) in 5 points of the sample and the device indicates the average of the results, which is subsequently taken into account in various calculations or comparisons.
2. Each sample (soap or cotton sample washed after soiling) is reproduced 5 times (under the same working conditions); then, its color is measured.
3. The data resulting from the 5 copies are used to calculate the color differences from the standard.
4. The arithmetic mean of the 5 color differences is calculated and, subsequently, so is the root mean square.

2.2.4. Analyses Indicating the Quality and Effectiveness of the Soap

Efficiency of Soaps Revealed After Washing the Soiled Samples

Five series of cotton samples are used, each sample with dimensions of 10 × 10 cm. A circle with a diameter of 1.5 cm is sewn onto each cotton sample with colored thread. In the center of the circle, a volume of 0.2 mL of very dirty engine oil, which is dark in color (black), is added with a micropipette. This delimitation is necessary so that the measurements after washing can be made inside the circle. The 5 series of dirty samples are washed for 30 min at 60 °C, 95 °C and 100 °C, respectively, using 100 mL of solutions formed by dissolving 1 g of soap in 100 mL of distilled water. The concentration of the washing solution is 1% (*w*/*v*). To determine the effects of washing the soiled sample, it is necessary to measure the color, L*, a* and b* and the reflectance R of the cotton samples, both before soiling, after soiling with engine oil, and after washing.

Using these data, the effects of washing cotton samples with the formulated soaps are calculated:

1. Hidden stain visibility after washing (Hs);
2. Soiling Additional Density (SAD);
3. Percentage cleanability (PC).

The calculation methods for these 3 effects are given by Equations (6)–(8):

$$Hs = [(L^*_{\text{before stain}} - L^*_{\text{after wash}})/(L^*_{\text{before stain}})] \times 100\ (\%) \quad (6)$$

$$SAD = \log\ (R_{\text{before stain}}/R_{\text{after stain and wash}}) \quad (7)$$

where R indicates the reflectance of the sample, determined on a spectro-photometer.

The degree of cleaning (anti-soiling, also called "soil release") or Percentage cleanability (PC), is calculated with Relationship 8 [70,71]:

$$PC = 100 \times (SAD_{stained} - SAD_{washed})/SAD_{stained}\ (\%) \quad (8)$$

The Presence of Residual Essential Oil in the Washed Sample

The presence of residual essential oil in the washed sample is determined using UV-VIS analysis of 10 mL ethanol solutions in which the cotton samples washed (at 60 °C and 95 °C, respectively) with the formulated soaps are immersed and left to stand for 30 min.

Method for Determining Antimicrobial Capacity

The textile samples (3 × 3 cm) are immersed in 2 mL of sterile physiological saline, distributed in sterile test tubes. The samples are vortexed for 1 min at 2000 rpm and subsequently incubated at 37 °C for 48 h. After this period, 1 mL is taken from each test tube and distributed in sterile Petri dishes, on top of which Mueller–Hinton Agar from Oxoid (Cheshire, UK) culture medium is added. After homogenization and solidification of the medium, the Petri dishes are incubated at 37 °C. Subsequently, after 48 h, the samples are examined to determine the number of microbial colonies (CFU—Colony-Forming Units/sample 3 × 3 cm/mL washing suspension) formed on and in the structure of the culture medium. By determining the microbial load of the tested samples, the antimicrobial efficiency of treatments applied to textile supports can be assessed, which do not allow for the attachment and multiplication of microorganisms from the environment.

2.3. Statistical Analysis

The statistical analysis consisted of calculating the working errors (expressed in percentages) to highlight the variability in the results and the precision of the measurements. In order to be able to make this calculation, each experiment was carried out in 5 copies. These errors are highlighted on each figure as vertical lines of different lengths according to the magnitudes of the error values obtained.

3. Results and Discussion

3.1. Characterization of Oils Used in Soap Formulation

The quality of the oils used in the production of soaps is given by the SAP, IN and INS values, influencing the quality of the soap. Thus, a high SAP value indicates that the oil is of good quality and contains a high proportion of fatty acids that are easily saponified because they have a shorter average chain length, and the triglycerides of which they are a part are characterized by lower average molecular weight values. The IN values give anticipatory indications on the final properties of the soap, such as cleansing capacity, texture, hardness, stability and durability. The INS is actually a way to quickly identify mixtures of triglycerides that saponify easily and give a hard soap.

For the formulation of natural laundry soaps, two vegetable oils are chosen for the following reasons: olive oil gives the soaps the best conditioning properties, and coconut oil generates the best cleaning properties.

Olive oil positively influences the soap's hardness bar, and contributes to the acquisition of a low foaming but gentle cleaning capacity. In addition, it provides a good conditioning and softening effect on human skin or laundry due to its high oleic acid content.

Coconut oil leads to a hard soap with a very high foaming capacity that determines excellent cleaning properties.

The addition of essential oil to the recipe can give the soap (depending on the type used) antimicrobial, antiseptic, disinfectant, antifungal effects and will also impart these effects to the textiles washed with these soaps. For this reason, these newly formulated

soaps can be used both at home and in the medical field for washing, disinfecting work equipment, blankets, towels, pajamas, and bed linen used in the hospital environment.

The SAP, IN and INS values are determined according to the methods described in the Section 2 and are shown in Table 2.

The quality of the oils implicitly influences the quality of the laundry soap:

- Coconut oil: It is a mixture of saturated (89%) and unsaturated (11%) fatty acids, of which lauric acid, myristic acid and palmitic acid predominate. The lack of double bonds in the chemical structures of some of the constituent fatty acids gives coconut oil a solid, white consistency [72]. In addition to fatty acids, coconut oil also contains other organic substances, such as phytosterols, vitamins (E and K) and antioxidants. The exact composition of coconut oil may vary depending on its origin and processing.
- Olive oil: Unlike coconut oil, unsaturated fatty acids predominate in olive oil (83%), the rest being saturated (17%). Olive oil is a greenish yellow liquid rich in oleic acid, which has 18 carbon atoms in the molecule and one unsaturation. The components of the polyphenol type, Tocopherols and Tocotrienols (Vitamin E), give olive oil important antioxidant capacities [73,74].

The quality of the oils used in the production of soaps is given by the SAP, IN and INS values (Table 2). For comparison, Table 2 also includes the SAP and IN values for standard oils, according to *Codex Alimentarius*. It is observed that these oils are used in this work to formulate organic soaps that have SAP and IN values close to those of standard oils, which indicates that their composition in saturated and unsaturated fatty acids is normal, i.e., close to the standards.

Table 2. Quality indices of oils used in the saponification process.

Vegetal Oil	Oil Percent [%]	SAP (mg KOH/g Oil)	$SAP_{standard}$ (mg KOH/g oil)	IN (g Iodine/100 g Oil)	$IN_{standard}$ (g Iodine/100 g Oil)	INS
Olive pomace oil	70.42	184.66	182–193 [75]	84.07	75–92 [75]	100.59
Coconut oil 76 degrees	29.58	256.23	248–265 [76]	11.536	6–11 [76]	244.694
Olive pomace oil + Coconut oil 76 degrees	100	205.83	-	62.61	-	143.22

In addition, the data in the table indicate high values for SAP corresponding to the mixture of the two vegetable oils (205.83 mg KOH/g oils), which means that the saponification capacities of the fatty acids in these oils are good.

A mixture of oils in which unsaturated fatty acids predominate is used, leading to an IN value of 62.61 g iodine/100 g mixture of oils. This falls within the range corresponding to obtaining a good soap in terms of hardness, cleaning capacity and stability (41–70 g iodine/100 g mixture of oils).

Since the INS value obtained is 143.22, it is found that the formulated soaps are obtained from oils that saponify easily, leading to hard soaps.

Another type of oil incorporated into the formulated laundry soaps is essential oil; Neem, Tea Tree and Thyme essential oils are used.

The composition of Euflora's Tea Tree essential oil [77] is as follows: Terpinene 1-ol-4 (30.00–48.00%), Terpinene gamma (10–28%), terpinene alpha (5–13%), cineol or eucalyptol (0–15%), paracymene (0.5–12%).

In this article, a Tea Tree essential oil which contains terpinene-4-ol (5–13%), p-mentha-1,4-diene (30%), eucalyptol (15%), alpha -terpinene (15%), p-cymeme (15%), alpha terpineol

(8%), terpinolene (6%), alpha -pinene (6%), myrcene (3%), β-phellandrene (3%) and d-limonene (3%) is used [78].

The composition of the Thyme essential oil used in the formulated laundry soaps is as follows: thymol 55%, p-cymene 40%, carvacrol 15%, linalool 8%, terpinene-4-ol 4%, and other components.

3.2. Confirmation of the Presence of Essential Oil in Soap

3.2.1. FTIR

Comparisons between soaps without essential oil, considering the standards (CS1 and HS1), formulated by hot and cold saponification, respectively, are shown in Figure 1.

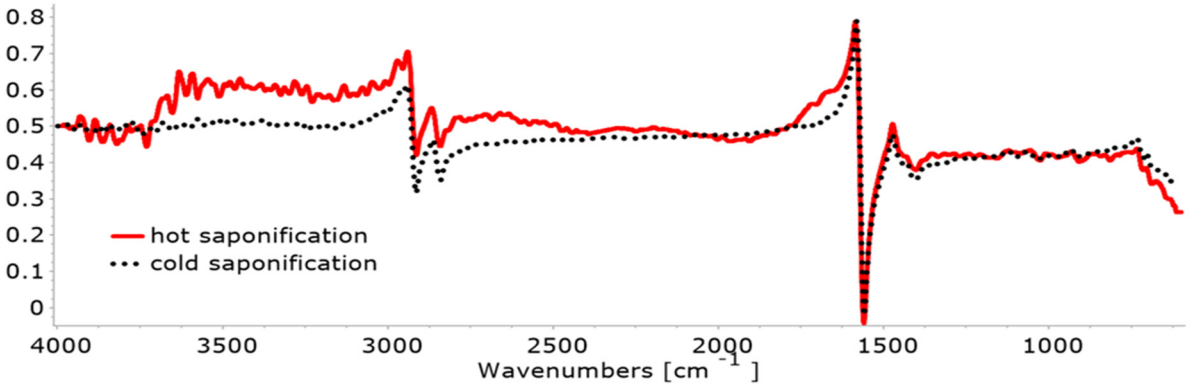


Figure 1. FTIR spectra of standard soaps (CS1 and HS1), made by hot and cold saponification.

Figure 1 shows that the heights of the overlapping peaks, from 1561 cm^{-1} (C-O stretch), related to the two saponification processes (hot and cold, after 1 month of ripening) are approximately equal, which means that cold saponification is a good option for soap formulation. Other significant peaks appear at 2941 cm^{-1} and 2861 cm^{-1} (symmetrical, and symmetrical stretching vibration of the methylene -CH_2 group), 2367, 1457 cm^{-1} (bending vibrations of the CH_2 and CH_3 aliphatic), 1438 cm^{-1} (deformation δC-H), 1396 cm^{-1} (bending vibrations of CH_2 groups). These are in agreement with the literature [79].

The presence of an essential oil in the soap mass can influence the appearance of the FTIR spectrum. In the case of cold saponification, the essential oils used in soap-making do not bring changes to the spectrum compared to the standard (without essential oil) (Figure 2).

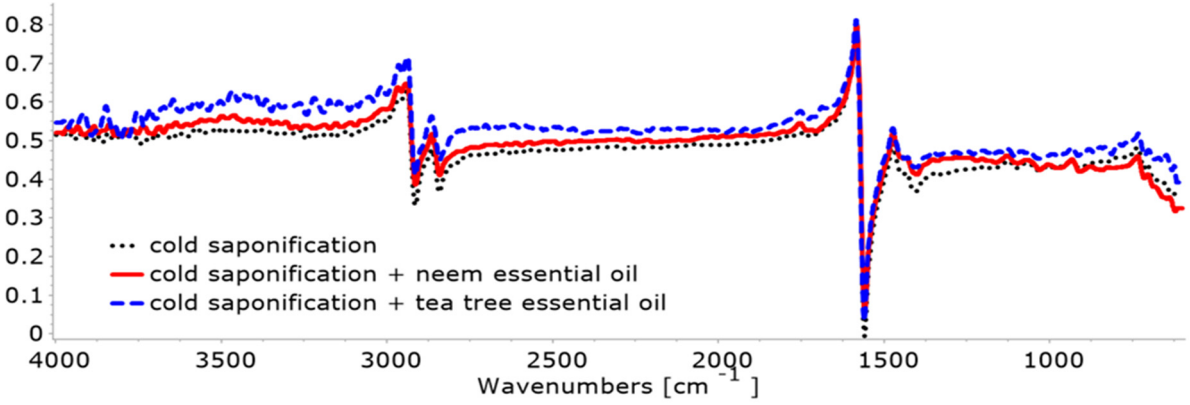


Figure 2. FTIR spectra of soaps formulated by cold saponification.

In Figure 3, the presence of essential oils in the hot saponification process brings about changes in the absorption bands in the ranges of 4000–3400 cm^{-1} (-OH groups in phenolic compounds or alcohols), 3000–2800 cm^{-1} (=C–H, trans and cis, symmetric stretching

C-H) and 1750–1550 cm^{-1} (-C=O stretching and $RHC=CH_2$ stretching in cis olefins) and 730 cm^{-1}. Tea Tree essential oil is rich in terpinene-4-ol and d-limonene, which absorbs strongly at approximately 730 cm^{-1} (attributed to aliphatic long chain hydrocarbons), 800 cm^{-1} (-HC=CH- (cis), bending (out of plane) specific to olefins), 885 cm^{-1} ($=CH_2$, out of plane deformation), 955 cm^{-1} (-HC=CH- (trans), out of plane deformation for disubstituted olefins) and between 2975 and 2925 cm^{-1} (corresponding to stretching vibration in the CH_2 aliphatic chain) [80]. Other weaker absorptions appear in the domains of 1022–1068 cm^{-1} (-C=O, stretching of ester groups), 1126 -1161 cm^{-1} (-C–O, C-OH, stretching, bending), 1379 cm^{-1} (-dimethyl, out-of-plane deformations in cis olefins), and 1442 -1465 cm^{-1} ($=CH_2$, deformation in plane) are observed [81].

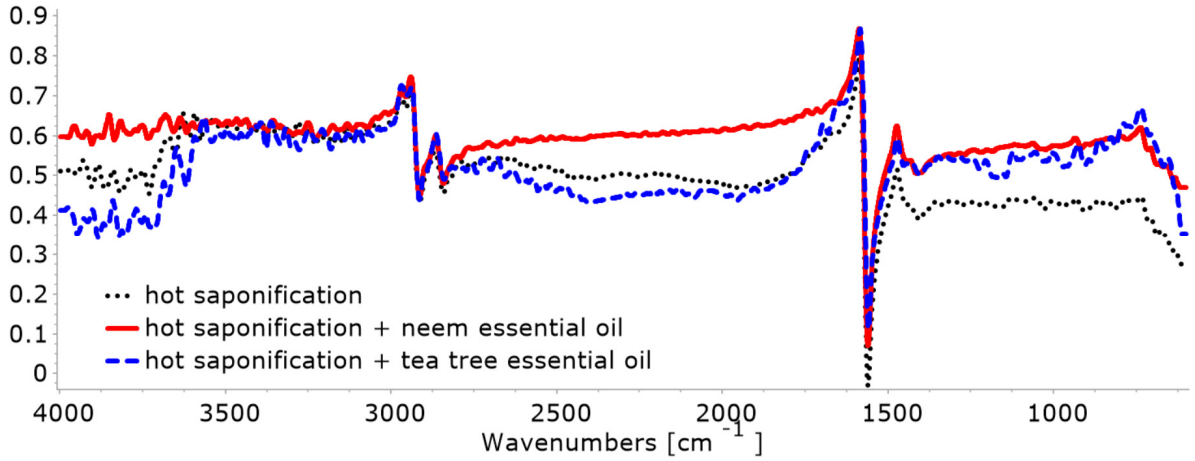


Figure 3. FTIR spectra of soaps formulated by hot saponification.

FTIR analysis of Neem essential oil indicates absorption bands at approximately 3445 cm^{-1} (stretching vibrations originated due to stretching of O–H groups for intramolecular hydrogen bond), 1595 cm^{-1} (stretching vibrations originated due to aromatic skeleton vibrations involving both C–C stretching), and 1354 cm^{-1} (stretching of C–H stretching, CH_2 wagging, CO, C–O bonds of acetyl esters, and C–O stretching) [82].

3.2.2. EDX Results

Elemental analysis of soaps indicates the presence of essential oils in soaps even after 8 months of their manufacture (Table 3).

Table 3. Elemental analysis of soaps.

		Norm. at %			
Saponification Type	**Atoms**	**Soap Without Essential Oil**	**Soap + Neem Essential Oil**	**Soap + Tea Tree Essential Oil**	**Soap + Thyme Essential Oil**
Hot saponification	C	39.36	39.57	39.81	39.71
	Na	9.98	9.42	9.33	8.79
	O	50.66	51.01	50.86	51.50
Cold saponification	C	39.70	39.85	39.92	40.49
	Na	9.27	9.29	9.20	8.62
	O	51.03	51.31	50.88	50.89

The changes occur due to the temperature during saponification, the mixing time, the mass of essential oil and due to the volatilization of some components of the essential oil included in the soap.

Compared to standard soaps (without essential oil), soaps containing essential oils contain more C atoms regardless of how saponification is performed: hot or cold. Hot-formulated soaps contain between 39.36 and 39.81% C atoms and cold-formulated soaps are richer in C atoms (39.70–40.49%). This fact demonstrates that cold-formulated soaps are a better option for formulating an ecological soap.

In addition, the decrease in the percentage of O in soaps containing an essential oil can be explained by the higher volatility of some of its components; some of the volatile components that also contain O atoms evaporate during hot saponification or during ripening, during the 8 months of storage, until the EDX analysis is performed.

The graphs related to the EDX analysis of each soap are presented in the Supplementary Materials, in Figures S1 and S2.

3.2.3. SEM Results

The surface appearance of each formulated soap is shown in Figure 4.

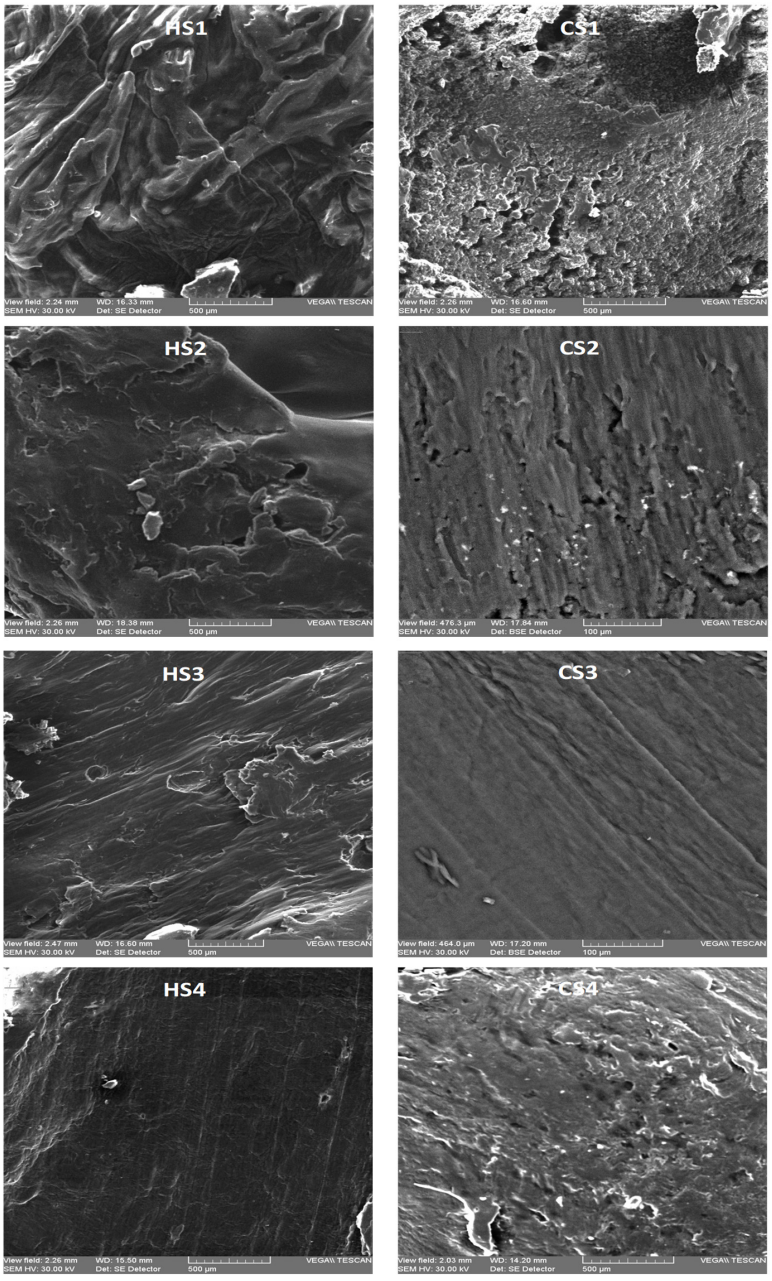


Figure 4. Electron microscope images of hot- (HS1–HS4) and cold (CS1–CS4)-formulated soaps.

SEM images indicate that hot-made soaps (HS1–HS4) have a more uneven surface appearance and are glossy compared to cold-made soaps (CS1–CS4). The final appearance of the soap is influenced by both the time for and the way in which the components are mixed (continuous/discontinuous and uniform) during saponification. When soaps are manufactured by the cold process, the mixing of the components participating in the saponification reaction leads to a homogeneous mass that can faithfully take the shape in which it is poured (Figure 4).

Each essential oil added at the end of the hot/cold saponification process improves the homogeneity of the mixture, probably due to the content of ketones and aldehydes that can dissolve certain fats. Among the essential oils used, Tea Tree oil has the best effect (in HS3 and CS3 soaps).

3.2.4. Elemental Mapping Results

The positions occupied by the chemical elements C, Na and O in each tested soap are shown by Map (elemental mapping) (Figures 5 and 6). This analysis is necessary to visualize the spatial distribution of the constituent elements in each soap.

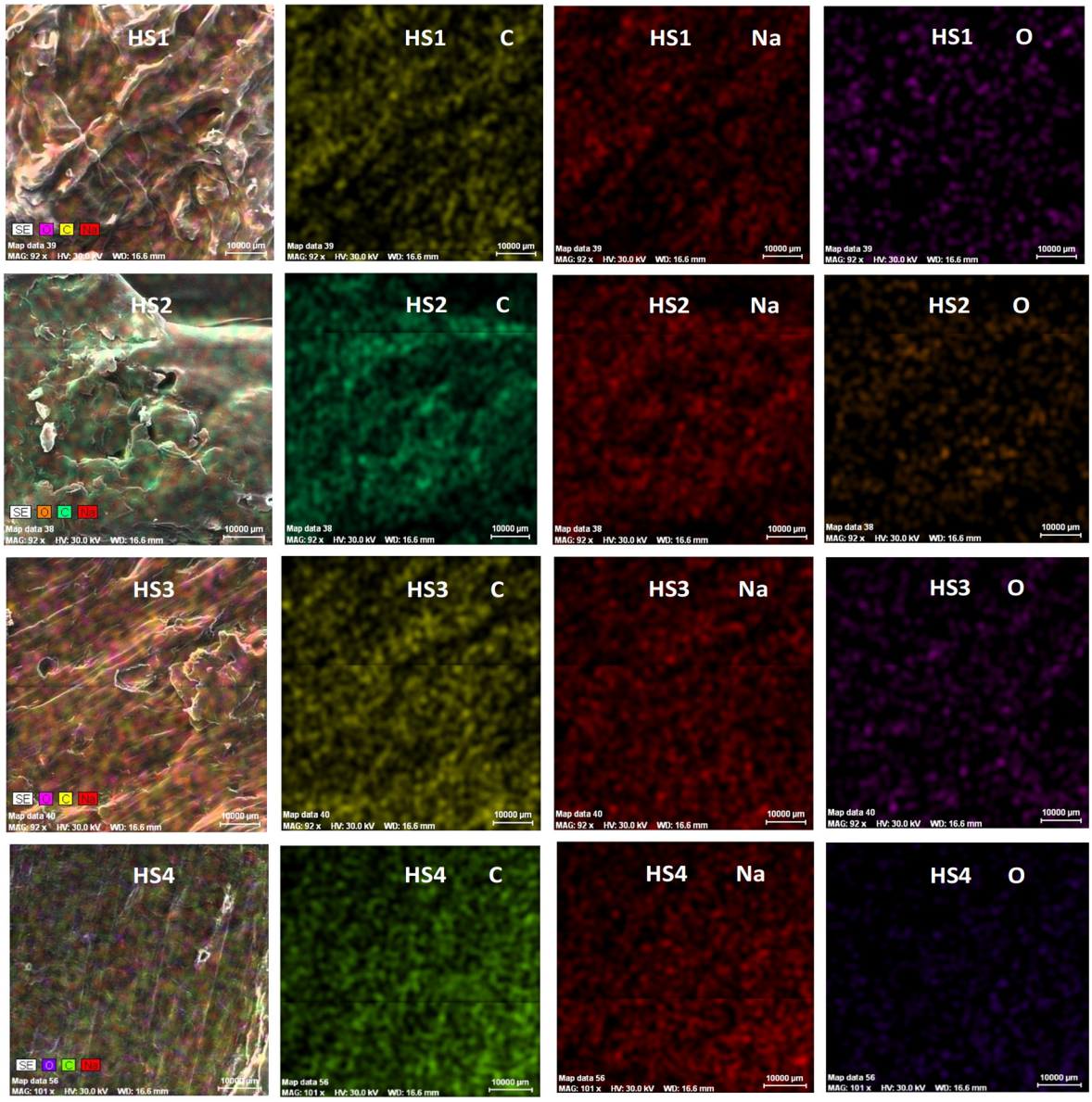


Figure 5. Elemental mapping for hot-formulated (HS1–HS4) soaps.

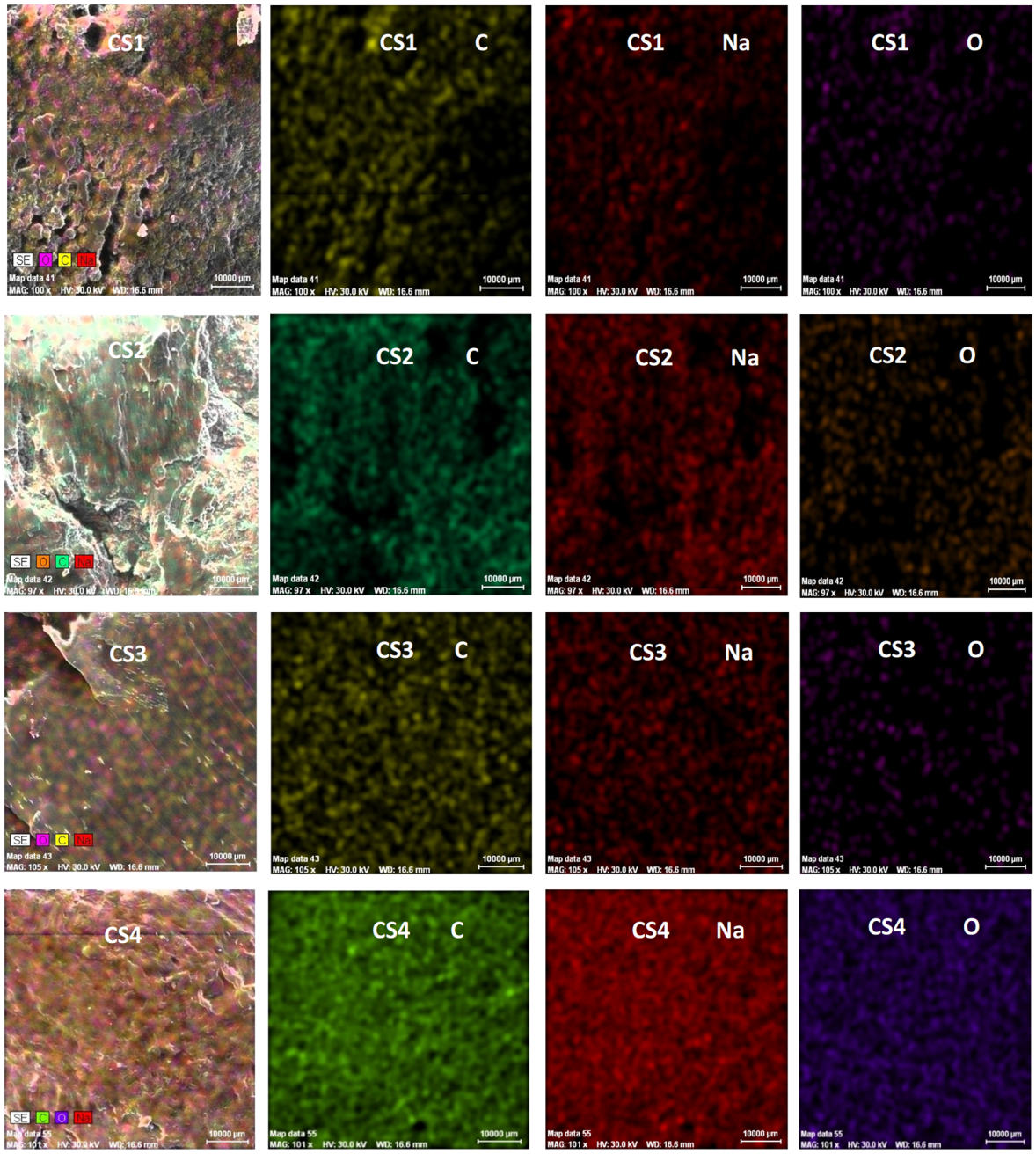


Figure 6. Elemental mapping for cold-formulated (CS1–CS4) soaps.

From Figures 5 and 6, it can be seen that the Na atoms (symbolized in red) are uniformly distributed in the soap, in close proximity to the O atoms, which most likely belong to the ester groups in the soap.

3.2.5. Thermal Analyses: Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

Analysis DTA (Figures S3 and S4) highlighted that the successive stages of the soap sample burning profiles are as follows: evaporation of moisture, volatile release, burning of the volatile compound in evaporation of moisture, volatile release/char formation, burning of the volatile hydrocarbon in the gaseous space, and combustion.

At the end of the thermal analysis, the higher values of the mass difference compared to the standards (without essential oil) formulated hot or cold are the results of the burning of the soaps but also of the volatilization/burning of the essential oils in the soaps (Table 4).

Table 4. Size of mass difference at the end of thermal analysis.

Soap Type	Loss of Soap Mass by Burning (mg)	
	Hot Saponification	Cold Saponification
Soap without essential oil	10	8.6
Soap with Neem essential oil	11	12.64
Soap with Tea Tree essential oil	8.7	11.71

Although hot saponification is more efficient, proceeding with a higher yield, after the burning of the soap a lower mass loss is still recorded compared to the case of the cold-formulated soaps. Cold saponification preserves the essential oil in larger quantities, which it eliminates during the burning of the soaps, leading to losses of up to 12.64 mg in the case of the soap containing Neem (Figure S4b).

The flash points of essential oils are lower than 100 °C: 55 °C for Thyme, 56.6–59 °C for Tea Tree and 76 °C for Neem, which is why they must be added after the completion of the hot saponification process to avoid their destruction. If the mass loss in the range 40–100 °C is analyzed (Figures S3 and S4), it is found that soaps containing essential oils record a greater mass loss (by 0.1–0.6 mg/50 mg soap) than the standard soaps, formulated hot/cold.

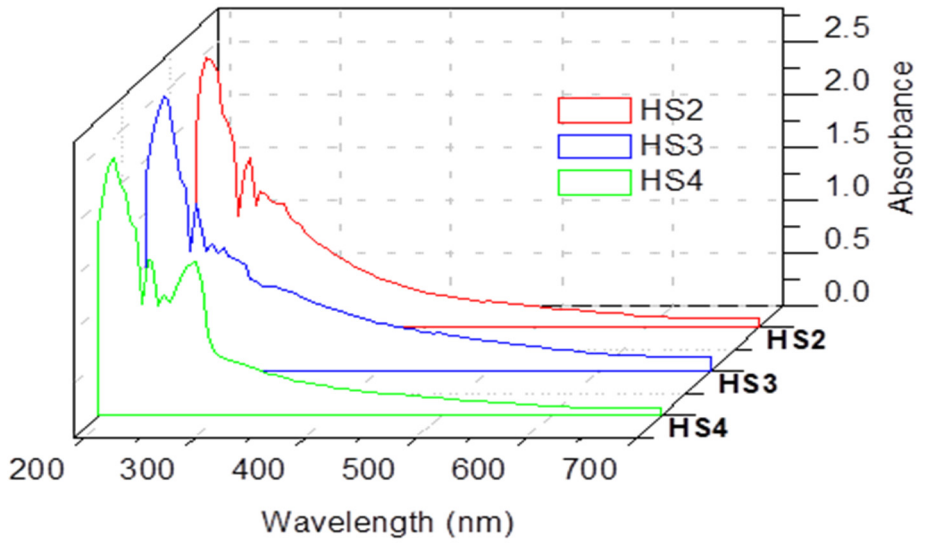
The temperature during the saponification and the duration of mixing the soap mass with the essential oil are two factors that must be taken into account. It can be said that the cold saponification method is preferable to the hot one because the low saponification temperature eliminates the risk of release of volatile compounds (such as terpene and aldehydes) from the essential oil used in soap formulation, thus maintaining, in the long term, both perfume and other properties induced to the soap.

It turns out that the main advantages and disadvantages of each soap formulation process, in terms of the effectiveness and properties of the soap that includes an essential oil, are the following [39,62]:

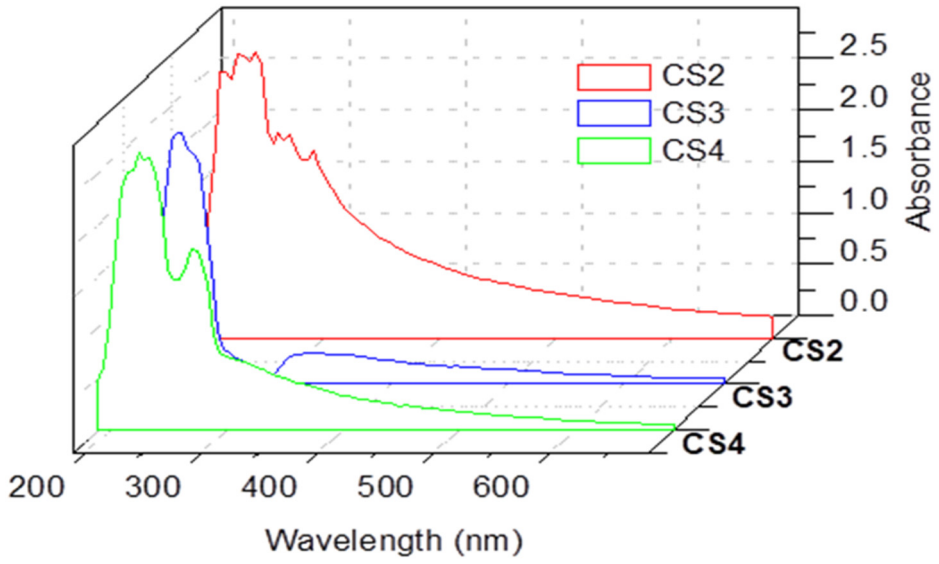
1. *In the case of cold saponification*: Ease of application, better control of the components in the recipe, no alteration in the quality of the base oils, and better preservation of the properties of the essential oils due to the preservation of compounds susceptible to volatilization because the processing temperature during saponification is low. As regards disadvantages: long ripening time (at least one month) and the risk of degradation of the base oils and essential oil during the ripening period, due to different storage conditions (air, humidity, heat, oxygen).
2. *In the case of hot saponification*, a ripening stage is no longer necessary, resulting in faster soap production. However, part of the volatile components of the essential oil evaporates even if their addition is made at the end of saponification, as the volatilization process cannot be controlled.
3. *In both saponification processes (hot/cold)*, glycerin is also a result of the reaction by-product, which, by not being removed, gives laundry soap the ability to improve the feel of washed laundry (as a fabric softener) and reduce electrostatic charge in textiles.

3.3. UV-VIS Results for Soap Solutions

To test the presence of essential oil in soap after 8 months of ripening, UV-VIS analysis of a 1% solution (made by dissolving 0.10 g of soap in 6 mL of saline and 4 mL of distilled water) is used (Figure 7a). The absorbance reading is made after dissolving the soap and maintaining the solution for 30 min at a temperature of 37 °C. Then, 3 mL of the solution made by mixing 6 mL of saline with 4 mL of distilled water is used as a standard.



(**a**)



(**b**)

Figure 7. Absorption of essential oils from: (**a**) hot-formulated soaps; (**b**) cold-formulated soaps.

The results in Figure 7a,b show the absorption bands characteristic of essential oils, in all soaps, obtained by both cold and hot saponification. Neem essential oil absorbs between 235 and 240 nm, Tea Tree essential oil at around 270 nm, and Thyme at approximately 285 nm. These wavelengths are extremely close to those indicated in the literature [53,83–85].

Tea Tree essential oils (from CS3) and Thyme (from CS4) are found in higher quantities in cold-formulated soaps because the saponification temperature does not favor their evaporation as it happens in hot saponification processes. Neem essential oil with a base note evaporates more slowly in the hot saponification process, but in the cold-manufactured soap, during the 8 months of ripening, the evaporation process takes place with a certain evaporation rate of this essential oil.

3.4. Soap Characteristics

The physicochemical characteristics of the tested soaps are compared with those of some soaps marketed in Romania, and the results are included in Table 5.

Table 5. Physicochemical characteristics of soaps.

Crt. No.	Soap Component	Soap Code	pH	Foam Height [cm]	L*	a*	b*
1	olive and coconut oils	CS1	9.95	9.5	71.57	−3.41	5.54
2	olive and coconut oils + Neem	CS2	9.82	9.5	63.00	−2.48	11.92
3	olive and coconut oils + Tea Tree	CS3	9.85	9.5	66.09	−3.58	6.62
4	olive and coconut oils + Thyme	CS4	9.82	9	59.78	−2.66	7.94
5	olive and coconut oils	HS1	9.97	16.5	68.65	−3.2	7.79
6	olive and coconut oils + Neem	HS2	9.74	9.5	59.42	−3.21	6.8
7	olive and coconut oils + Tea Tree	HS3	10.1	12.5	65.56	−3.51	7.71
8	olive and coconut oils + Thyme	HS4	9.9	14	57.00	−2.87	6.97
9	100% olive oil cold-formulated	CM	9.74	8	78.26	−3.28	−8.68
10	100% coconut oil cold-formulated	CC	9.755	7	69.46	−2.35	−5.68
11	detergent A	CDA	9.805	1	86.85	0.22	−0.09
12	detergent B	CDB	7.96	0.5	80.96	0.55	1.16
13	ChanteClair soap	CCh	9.7	7	48.43	−3.42	0.41
14	Popular soap	CP	9.215	9	90.44	−1.11	5.75
15	Fairy detergent	CF	8.325	5	75.68	−4.31	42.54
16	100% olive oil hot-formulated	HM	9.76	8.5	76.52	−2.83	12.76
17	100% coconut oil hot-formulated	HC	9.255	15	83.06	−0.14	4.90

It is observed that, by dissolving soaps (Nos. 1–8 in Table 5), a pH around 10 is generated; the soaps used for comparison (Nos. 9–17 in Table 5) present lower pH values, starting from 7.96 to 9.85. Hot-formulated soaps generate a more consistent foam than cold-processed ones, regardless of the stirring/testing time; the highest foaming capacity is that of the soap made from 100% coconut oil through the hot saponification process. The other soaps used for comparison have a much lower foaming capacity (1–8.5 cm foam height) after stirring the solution for 10 s.

The measurement of the soap colors indicated the following aspects: cold-made soaps (CS1-CS4) are brighter, with higher L* luminosities (L* ranging from 71.57 to 59.78), than the other hot-made soaps (L* = 57–68.65); the soaps used for comparison have higher luminosities than the tested soaps, with the exception of ChanteClair soap (L* = 48.43), which is a Marseille soap formulated with olive oil. The blue tints are more pronounced in the cold-made soaps, with a* values ranging between −3.41 and −2.48. However, the tested formulations retain a yellowish tint, originating from the olive oil, with b* values ranging from 11.92 to 5.54.

3.5. The Ability to Clean Fatty Dirt

The ability to remove fatty dirt from cotton samples can be appreciated both qualitatively and quantitatively.

The qualitative assessment of the presence of residual stains (visibility of residual dirt), after washing with soaps made by hot or cold saponification, can be carried out with two tests:

1. The color staining test (according to AATCC 130-2000 [86] or ISO 6330-2012 [87]), which evaluates the visibility of oily dirt after a washing with soap, during home laundering;
2. The value of the CMC color difference (which is based on the colorimetric principles of the CIE 1976 system) to appreciate the tolerance of the "residual stain" to the cotton sample before dirt. The CMC test stipulates that between the tested sample (dirty but washed with soap) and the control test (before dirt), there should not be

a color difference greater than 1. The conclusion of the CMC test is expressed by a qualification: PASS or FAIL [88].

The data obtained in the case of the formulated soaps are included in Table 6.

Table 6. Color staining values and decision of CMC color difference (compared to white, before dirt).

Saponification Type	Soap Code *	Color Staining After Washing at the Temperature of: **			CMC ***
		60 °C	95 °C	100 °C	
Cold saponification	CS1	4	4–5	4–5	FAIL
	CS2	3–4	4–5	4–5	FAIL
	CS3	4	4–5	4–5	PASS
	CS4	4	4–5	5	PASS
	CM	4	4–5	4–5	FAIL
	CC	4	4	4–5	FAIL
Hot saponification	HS1	4	4–5	4–5	PASS
	HS2	4	4–5	4–5	PASS
	HS3	4	4	4–5	PASS
	HS4	4	4–5	4–5	PASS
	HM	4	4–5	4–5	FAIL
	HC	3–4	4	4–5	FAIL
	CDA	3–4	3–4	3–4	FAIL
	CDB	4	4	4	FAIL
	CCh	4	4–5	4–5	FAIL
	CP	4	4–5	4–5	FAIL
	CF	3–4	4	4	FAIL

* Soap code used to wash the cotton sample; ** color staining (according to AATCC 130-2000 [86] compared to white sample) after washing at 60 °C, 95 °C or 100 °C; *** decision of CMC color difference (compared to the white sample before dirt).

The results indicate that the best values are obtained after washing at 100 °C when the oil stains are no longer visible, and the notes received after the evaluation (according to ISO 6330-2012 [87]) are 4–5 or even 5, in the case of using the CS4 soap.

CMC color difference is a useful measure of the commercial acceptability of colored products. As after staining, the samples are intensely colored in black brown and, after washing, the color disappears, it is important to quantify the color difference compared to the standard sample. It is observed that the white on the standard sample is extremely close to the white cotton samples washed with the CS3, CS4 and HS1, HS2, HS3 and HS4 soaps, which is why they passed the CMC test.

The quantitative appreciation of the cleaning capacity manifested by the soaps is achieved by determining *Hidden stain* (Hs) as a visibility after washing, *Soiling Additional Density* (SAD) and *Percentage cleanability* (PC) (Figures 8–10).

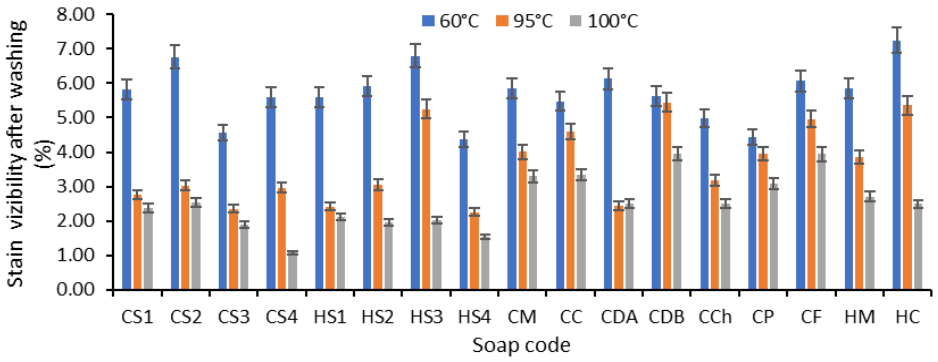


Figure 8. Hs values after washing cotton samples at different temperatures.

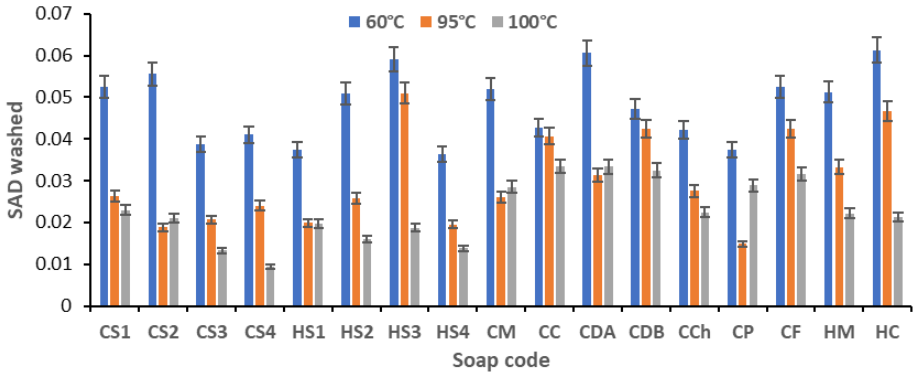


Figure 9. SAD values after washing cotton samples at different temperatures.

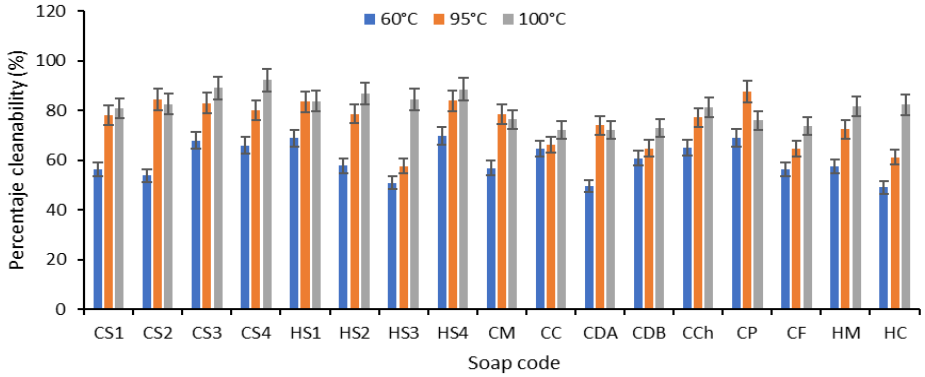


Figure 10. Percentage cleanability of soaps.

Hs (Hidden Stain/Stain Visibility after Washing) has the lowest values when washing is performed at 100 °C (Figure 8). The soaps containing Thyme essential oil have the best dirt removal capabilities by recording the values Hs = 1.07% for CS4 and 1.54 for HS4. The lack of essential oil (in CS1 and HS1) determines the attainment of higher Hs values (2.38% in the case of CS1 and 2.12% in the case of HS1). Washing at 95 °C leads to values very close to those obtained at 100 °C but slightly larger. If the washing temperature is even lower (60 °C), the Hs values vary between 4.56 and 6.76% in the case of cold-manufactured soaps and between 4.38 and 6.79% in the case of hot-manufactured soaps.

It is known that the smaller the SAD values, the higher the cleaning capacity of the soap.

When washing of the cotton samples is carried out at 100 °C, the SAD washed values in the case of cold-formulated soaps decrease with the addition of the essential oil as follows: 0.02297 for CS1, 0.02103 for CS2, 0.013255 for CS3 and 0.009419 for CS4 (Figure 9). The soaps formulated by hot saponification are more efficient, leading to lower SAD values: 0.019652 for HS1, 0.016087 for HS2, 0.018717 for HS3 and 0.013853 for HS3. It is found that the essential oil included in the soap increases its ability to clean the fatty dirt.

Washing at 95 °C leads to slightly higher values, but extremely close to those obtained at 100 °C washing.

Of all the tested soaps, the best cleaning capacities are shown by the CS4 and HS4 soaps when washing is performed at about 100 °C, because the PC values are of 92.16 and 88.47%, respectively (Figure 10).

In all tests (Hs, SAD and PC), the addition of essential oil leads to a greater removal of the engine oil with which the samples were intentionally stained. Soaps containing Thyme essential oil are the most effective.

3.6. The Presence of Essential Oil in Soap-Washed Samples

Ethanol is used as a solvent to capture the residual essential oil remaining in the samples washed with the formulated soaps. The cotton samples, washed with soap, rinsed and dried, are stored in 10 mL ethanol for 30 min. At the end of the storage, the ethanol mixture and residual essential oil are analyzed on a UV-VIS spectrophotometer, using 3 mL of ethanol as a standard. The absorptions of residual essential oils are indicated in Figure 11.

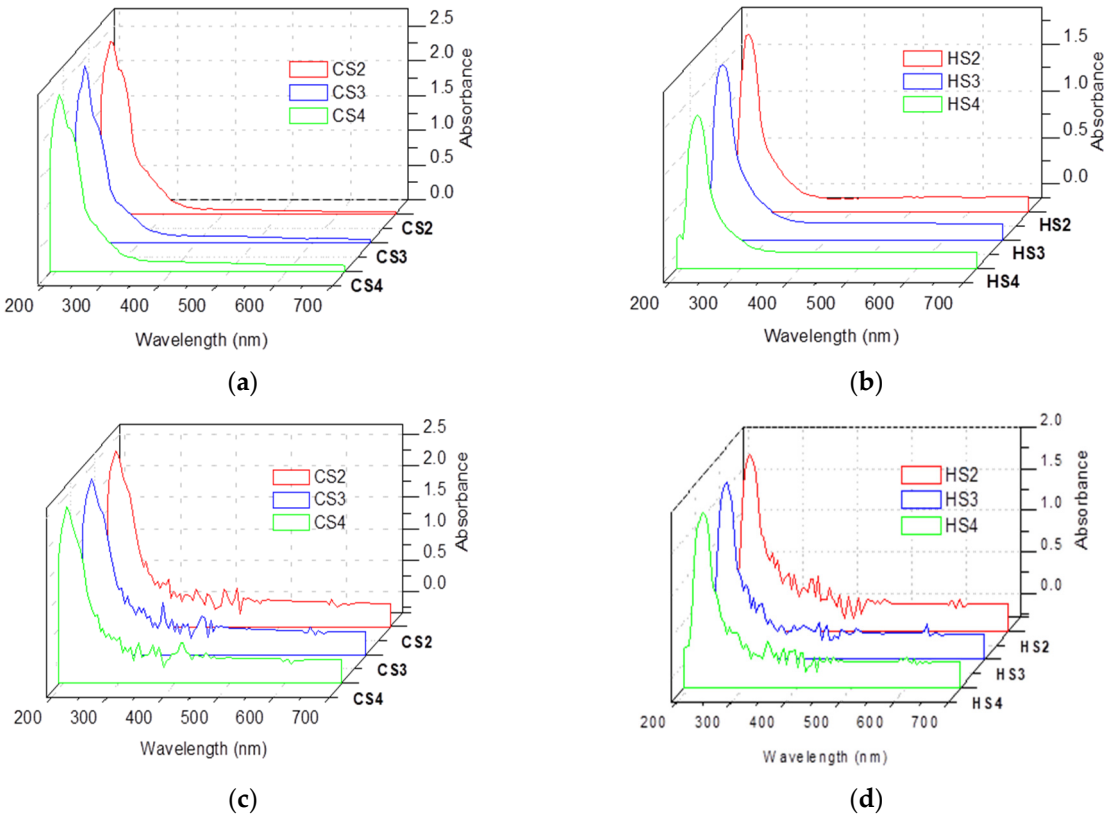


Figure 11. Absorption curves of ethanol solutions that have residual oil from cotton samples washed at 95 °C (**a**,**b**) or 60 °C (**c**,**d**), with cold-formulated soaps (CS2, CS3 and CS4) or hot-formulated soaps (HS2, HS3 and HS4).

In Figure 11a,b, it can be observed that the high temperature (95 °C) during the washing of the cotton samples leads to a large evaporation of the essential oil because it exceeds their flash point (55–76 °C). Only in the case of the use of cold-formulated soaps are slight changes observed, at the wavelengths at which the three essential oils absorb. The same observation is not made when the washing test is performed at a lower temperature, 60 °C (Figure 11c,d). On the curves, there are several drops, including those characteristics of the basic component of each essential oil: 248 nm for Neem, 237 nm for Tea Tree, and 285 nm for Thymol.

It is known that laundry is washed at 100 °C only exceptionally; normally, for washing, temperatures of 40 °C or maximum 60 °C are preferred. It is found that washed laundry keeps traces of soap and essential oil no matter how intensely they are rinsed. The latter manifests disinfection effects, antimicrobials, as evidenced in the subsection titled "Antimicrobial Capacity".

The persistence of essential oils in cotton samples washed with CS2–CS4 and HS2–HS4 soaps depends on several factors: the quality of the essential oil, its volatility, the concentration used in the soap, the saponification method (cold or hot), the affinity of the textile

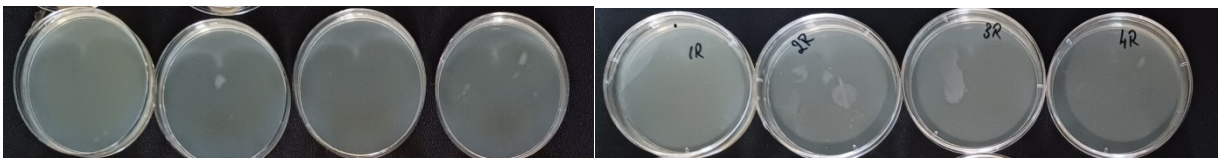
material for the essential oil, and the temperature used when washing and drying the textile material washed.

3.7. Antimicrobial Capacity

The determination of the total number of germs/products is made by a quantitative method and the results are shown in Figures 12 and 13 and expressed quantitatively in Table 7. Antimicrobial efficacy testing is conducted by assessing the ability of microorganisms to attach to and persist on the sample surface upon contact. Essentially, each sample serves as a potential support for bacterial biofilm formation.

(**a**) (**b**)

Figure 12. The results obtained after incubating for 48 h at 37 °C of textile samples washed with hot-formulated soaps, HS1–HS4 (**a**), coded as 1C–4C on the lids (**b**).



(**a**) (**b**)

Figure 13. The results obtained after incubating for 48 h, at 37 °C of the textile samples washed with cold-formulated soaps, CS1–CS4 (**a**) coded as 1R–4R on the lids (**b**).

Table 7. Results of antimicrobial analysis expressed in Colony-Forming Units (CFUs).

CFU */Sample 3 × 3 cm/mL Washing Suspension	
Soap Code (Number on the Lid)	**CFU ***
CS1 (1R)	0
CS2 (2R)	0
CS3 (3R)	0
CS4 (4R)	0
HS1 (1C)	1
HS2 (2C)	0
HS3 (3C)	0
HS4 (4C)	0

* CFU = Colony-Forming Units (Colony-Forming Units/sample 3 × 3 cm/mL washing suspension).

The sample is immersed in physiological saline, where vortexing is used to release any saprophytic microorganisms that may be present in the or on the textile sample at that moment. The resulting suspension is then introduced into Mueller–Hinton Agar, a culture medium recommended by international standards (EUCAST, CLSI) for antimicrobial testing.

By incorporating the suspension into the agar medium—melted, cooled to 45 °C, and homogenized with the vortexed suspension—the conditions are optimized for the growth of all potential microorganisms present on the sample surface. The absence of microbial growth confirms the efficacy of the applied treatments, which prevents microbial colonization and development on the textile sample surfaces.

The treatments applied to the test samples imprint the textile matrices' physicochemical properties that do not favor microbial multiplication. However, the exception is the sample washed with the HS1 standard soap (without essential oil, code 1C (on the lid) in Figure 12; 1 CFU/mL washing suspension). In the HS1 case, the explanation takes into account the long saponification time (1 h) at 100 °C, which may reduce the antioxidant and antimicrobial properties of olive oil during saponification. In contrast, in the case of CS1, the low cold saponification temperature (30 °C) does not affect the components responsible for the antimicrobial effects (polyphenols, lauric acid and vitamin E).

For comparison, the testing of the soaps formulated by hot/cold saponification, from 100% olive oil and 100% coconut oil, showed that all have antimicrobial effects, except for the soap consisting of 100% olive oil from hot saponification (the result being 1 CFU/mL washing suspension). HM soap formulated by hot saponification with 100% olive oil allows for the multiplication of microbes because prolonged exposure to 100 °C causes the degradation of the oil and, consequently, cancels the slight antimicrobial activity that olive oil normally possesses. In the case of HC soap, hot processed from 100% coconut oil, thermal degradation cannot cancel the strong antimicrobial capacity specific to lauric acid that predominates in coconut oil.

It is observed that all cotton samples washed with hot/cold-formulated soaps that have essential oil included in their mass opposed the multiplication of microbes.

3.8. Limitations

Although this study highlights the positive results of soaps formulated with olive oil, coconut oil and an essential oil, it also has several limitations:

1. It does not account for the long-term instability of volatile essential oil components in the soaps;
2. Dermatological testing is absent, which would be beneficial since laundry can be washed both using an automatic washing machine and by hand;
3. The lack of antimicrobial capacity testing in clinical settings;
4. Lack of a calculation regarding economic efficiency.

4. Conclusions

The novelty of this article consists of the design of saponification recipes and the way in which the cleaning capacity of the formulated soaps is highlighted. Thus, by choosing two types of vegetable oils, in certain proportions, in which saturated fatty acids predominate (in coconut oil) or are in small quantities (in olive oil), the aim is to balance some antagonistic effects given by these oils so that the final quality of the soaps can be good in terms of cleaning capacity, hardness, texture, foam, smell, stability and durability during storage.

Using vegetable oils (70.42% (*w*/*w*), olive pomace oil and 29.58% (*w*/*w*) coconut oil 76 degrees), ecological soaps are formulated, by hot and cold saponification. The SAP value of the oil mixture is 205.83 mg KOH/g oils, which means that the oil mixture has a good saponification capacity of triglycerides; the low value for the IN (62.61 g iodine/100 g oils) indicates that the soaps contain unsaturated fatty acids in small quantities, saturated fatty acids in large quantities, and the resulting soap tends to exhibit greater hardness. The low IN values confirm that the rancidity phenomenon, which is usually associated with a change in color towards brown, does not occur during long-term storage.

The inclusion of an essential oil (Neem in CS2 and HS2), Tea Tree (in CS3 and HS3) and Thyme (in CS4 and HS4), increases the washing capacity of the soap and confers antimicrobial effects, preventing microbial multiplication. The results of UV-VIS analyses confirm the presence of the essential oil both in the soaps dissolved in saline and in cotton

samples washed with these soaps by analyzing the ethanol solutions in which the washed (at 60 °C or 95 °C) and rinsed (several times) cotton samples are kept.

The excellent washing capacities of the formulated soaps, by hot or cold saponification, are demonstrated by very low Hs values and very high values for PC: Hs takes values between 1.07% and 2.53% after washing with CS4 and CS2, and 1.54% for HS4 and 2.12% for HS1. The cleanability power (expressed in percentage) is 92.16% when using the CS4 soap, and 88.47% when using the HS4 soap; the other soaps lead to PC values ranging from 88.47 to 92.16%.

The HS1, HS2, HS3, HS4, CS3 and CS4 soaps passed the CMC test, which means that the color difference between the cotton sample before being soiled with used engine oil and the color obtained after washing with these soaps are of less than 1.

Being sodium salts, the formulated soaps dissolve in water; they generate alkaline solutions (pH close to 10), and moderate foam after shaking, as is characteristic of laundry soaps used in washing machines. The color of the hot- or cold-formulated soaps is slightly yellowish-greenish (from the color of the predominant oil, olive pomace oil) and did not change.

With these physical and chemical characteristics, the formulated soaps could be used for washing clothes at home or even in hospitals to destroy microbes and disinfect sheets, pajamas, blankets, and other textiles in the operating room. However, before using them in hospitals, further research is needed to identify the types of microbes and fungi that these soaps can destroy.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app15073821/s1, Figure S1: EDX plots for hot-formulated soaps; Figure S2: EDX plots for cold-formulated soaps; Figure S3: TGA and DTA spectra of hot-formulated soaps; Figure S4: TGA and DTA spectra of cold-formulated soaps.

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