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Journey From Synthetic Cleaning Agents to Green Cleaning Agents- Review

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Abstract

Cleaning reagents are a common substance in every household and are used in everyday lives especially after the outbreak of COVID-19 around the world. This has been a part of households for hundreds of years. It is essential to remove dirt and germ not only from the clothes but also from the human skin. It is also used to remove stains, dust or unpleasant odor from the body and the clothes. These are available in various forms such as powders, granules, liquids and sprays. Cleaning reagents are generally manufactured by two ways that is using naturally available ingredients and the other is through using synthetic materials. Most frequently used synthetic cleaning agents are soaps, detergents, body cleansers etc. Soap water or detergent water which is non-biodegradable as well as toxic by nature is generally directly disposed through sewage lines thus adversely affecting the environment. So, it becomes necessary to replace these harmful cleaning reagents with the greener ones to reduce the harmful influence on the environment. Some of the green cleaning reagents are natural soaps, homemade products such as baking soda, lemon juice etc., vegetable oils and plant and fruit extracts, HNT, microbial cleaning, bio surfactants, plants-based surfactants.This review article aims to focus on the greener cleaning reagents

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which can be great alternatives comparatively to the present harmful cleaning reagent for the better effect on the environment and for human safety.

Keywords: Cleaning reagents, Synthetic cleaning reagents, non-biodegradable, toxic chemicals, green cleaning reagents, environment

History

Cleaning is the process which is practiced by the living beings to remove dirt and/or dust from the body or from other substance. In the past it was usually done only with the help of universal solvent that is water. Later various reagents such as soap, detergents were used. Around 2800 B.C.E. the world's first soap was accidentally created by ancient Babylonians where the combination of animal fat and wood ash with water was used to clean cooking utensils. Also, (around 5000 BC) the ancient Egyptians who were the first people to use soap to clean their clothes and their body regularly; added alkaline salts to vegetable and animal oil to create substance like soap for washing their clothes and body [1]. They even used bleach to whiten the clothes and other linens. The word "soap" was first coined from the Roman legend about mount Sapo where the rain water which washed down from the mountain, mixed with animal fat and volcanic ashes creating a clay like mixture, which was again discovered by accident. The water containing this clay like mixture went in the river Tiber which cleaned the clothes more effortlessly than normal water. The presence of natural surfactant in the animal fat helped to act like soap [2].

In 1889, Lever Brothers Company registered the trademark name 'Sunlight' in all countries. Sunlight was world's individually packaged laundry soap. In the year of 1898, B.J. Johnson produced the first liquid soap-Palmolive which had olive oil and palms as its constituents. In India, first soap manufacturing plant was developed in the year 1897 in Meerut, Uttar Pradesh.

The first indigenous soap was introduced by Mr. Jamshedji Tata in the year of 1918.

Figure 1: Chronological order of the development of soap through the era

Animal fats were used to make soaps during World War I (WWI) but were in less quantity which resulted in the formation of first synthetic detergents [1]. In 1928, the German firm H.T. Bohme produced the first commercial synthetic detergent products. Propylene, one of the components in detergents, was readily available from refineries after the Second World War. Also, petrochemical industries developed during this era which led to the modernisation of production and utilisation of domestic cleaning agents was observed also synthetic detergents overtook the use of soaps. Although being first produced in German during WW1, it was manufactured in America during early 1930s [5]. All-purpose detergent was formed by end of the year 1946, which was Tide by Gamble and Procter which became the overnight sensation. In developed countries, around 1950s, detergents replaced the use of soaps for washing clothes. In 1990s, liquid detergent with thick consistency was produced and in 2000, biodegradable, eco-friendly products came to use [1]. Till date many cleaning reagents have surfaced up where all of them generally fall into 4 distinct categories which are detergents, degreasers, abrasives and acids.

Introduction

Cleaning is the basic practice which we are totally accustomed with; whether it is washing the dishes, doing laundry, personal hygiene, ceramic sanitary facilities or washing of vehicles. These are done by using cleaning reagents which are used regularly in our day to day lives can be made synthetically i.e. products which are made with chemicals and naturally. The utility of the cleaning reagents increased drastically after the global pandemic of Coronavirus from mid-March in the year 2020. We use the synthetic cleaning reagents which includes mainly soaps and detergents whose role is to solubilize the insoluble impurities, collecting dirt and carrying it away with water. Both soap and detergent have surfactant as their surface-active reagents. Syndet or synthetic soaps are made from blends of plasticizers, synthetic surfactants, petrochemicals, artificial dyes and fragrances, binders and other additives [6]. The soap is the sodium or potassium salts of fatty acids of long carbon chain.

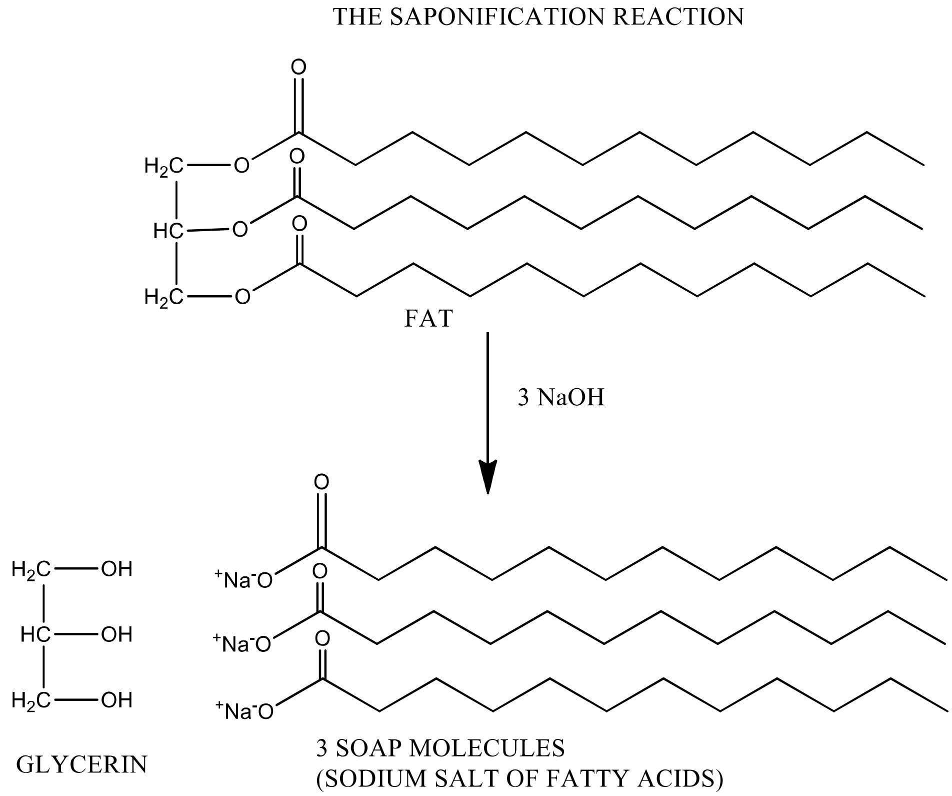

Figure 2: Reaction for the formation of soap molecules with glycerin as side product

The molecules of soap have two different properties that are hydrophobic and hydrophilic. The hydrophilic part interacts with the water whereas the hydrophobic tail of soap interacts with hydrocarbons [7].

There are various types of soap which includes

I. Toilet Soaps
II. Medicated soaps
III. Floating soaps
IV. Shaving Soaps
V. Soap chips

Firstly, toilet soaps which has artificial perfumes and dyes added to it and is made up of fatty acids and high-quality oil. Yearly usage of the soaps by one person in India is 1 kg against 6kg in USA,1 kg in Brazil, 2 kg in Indonesia and 4 kg in China (round figures).

Secondly, medicated soaps have antiseptic as one of its constituents. It helps to kill bacteria from the surface. Third, there are the "floating soaps," or soaps that float rather than sink. Before they set in their moulds these soaps are aerated in the soap mixture. Fourth, because glycerol is a component of soap, it doesn't dry out quickly. It is used for shaving. This type of soap has rosin which helps to form lather for shaving. Lastly there is soap chips which are left over fragments of soap formed during the production of soap. [8]. Other than a bar of soap there are also various forms of soap which are used for cleaning which includes shower gels, liquid dish soap for cleaning utensils, liquid detergents for washing clothes. Like soaps, synthetic detergent also works to clean the clothes and also have alike structures and properties. They are available as powdered or in condensed solutions. Compared to soaps they can work well in acidic or alkaline solution and both in hard water and soft water. They are soluble in hard water because of the polar sulfonate in detergents than the polar carboxyl of soap to bind with the ions present in hard water such as Ca2+. These are also known as 'soap less soap'[9]. A typical detergent formula contains more than one surfactant. The molecules of detergent molecules have long hydrocarbon chain and water-soluble ionic group. There are three types of detergents which includes: –

I. Anionic detergents
II. Cationic detergents
III. Non-ionic detergents

Anionic detergents are sulphate salts of long chain of hydrocarbons where the anion part acts as cleaning agent. Anionic surfactant widely used due to its low cost such as Alkyl phenols. Other surfactants are branched (BAS), which are non-biodegradable, and linear (LAS), which are both classified as alkylbenzene sulfonates. LAS is mostly used for cleaning in detergents.

In case of cationic surfactants, they have cationic charge heads which acts not only as good cleaning reagent but also carry germicidal properties. These detergents are ammonia salts of chlorides or acetates.

It is present in cleaning plastics, fabric softeners, conditioners and hair shampoos whereas non-ionic detergents do not carry any ionic head which make them unable to react with ions of hard water.

Non-ionic detergents are produced by reacting polyethene glycol with stearic acid. Example: glycosidic and polyoxyethylene. It is used in car shampoos, cosmetics and dishwasher detergents. [10].

Apart from synthetic detergents, surfactants are also present in shampoos, toothpaste and also have plentiful uses in industries. These detergents have good cleaning power due to the presence of phosphates.

Other than soaps and detergents, there are other cleaning reagents which are used for cleaning purposes are degreasers, acid and abrasives.

The role of degreasers is to eliminate water insoluble substances such as oils, proteins, grease and fats which is known as emulsifying so it has higher pH or turns alkaline. There are two types of degreasers- first is water-based degreasers which are non-inflammable and use water which makes them less damaging to the environment. It removes grease and layer is formed on top of wastewater. Other one is solvent- based which can be both flammable and inflammable. These are used in industries. For example: kerosene, trichloroethylene (TCE), petroleum ether, n-hexane etc. [11]

Acids have a pH lower than 6 which ranges from mild to very strong. Some edible substances which are acidic are lemon, vinegar, cola, coffee. These can be used for cleaning purposes too as it helps to remove difficult stains.[12]

Abrasives are the cleaning reagents which removes dirt from the substances by scouring effect. It is composed of chemical precursors which includes synthetic diamond, silicon carbide and alumina which is a synthetic form of corundum. It is usually used in the kitchens and garages. It can be also used to prevent rusting as it forms a thin protective layer which shields the surfaces from the elements. They are available in powdered form as well as liquids and also in form of scouring pads. Example of abrasives are salts, powdered borax, baking soda, materials like copper, steel, nylon and wool and minerals like silica, feldspar, calcite etc. The brusqueness of these abrasives depends on the various products and sometimes based on colour coding. [13].

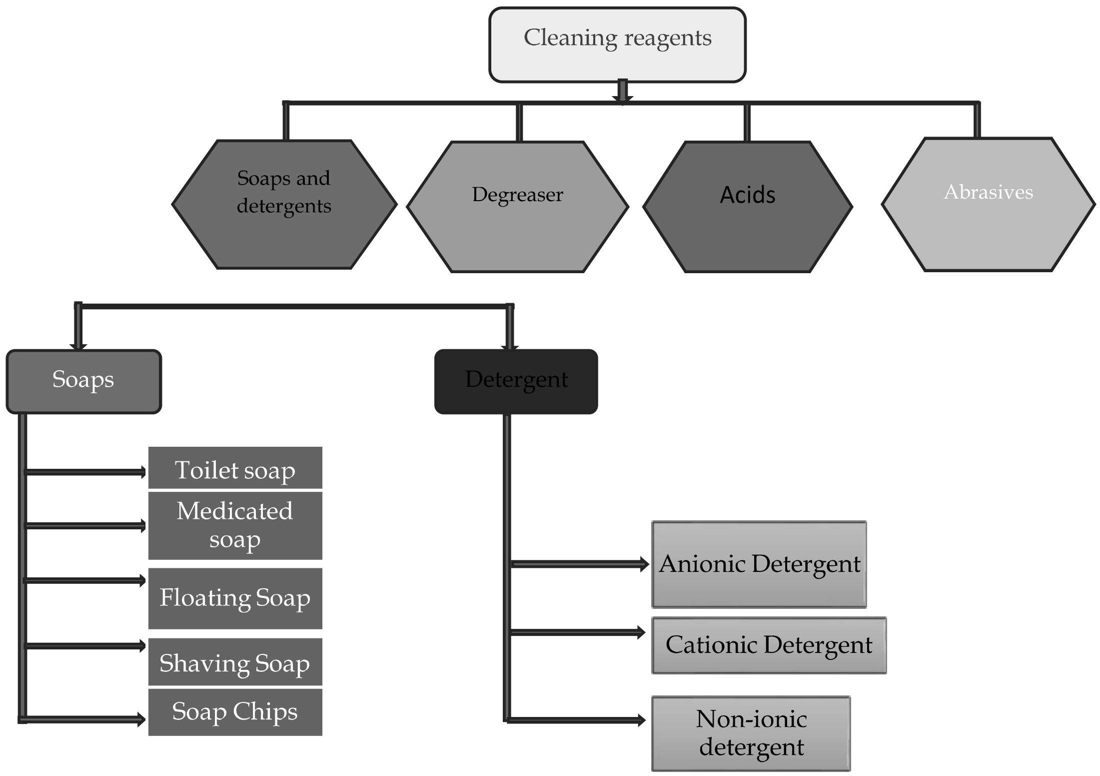

Figure 3: Chart representing types of cleaning reagents and its subgroups (of soaps and detergents)

Manufacturing Process:

Soaps

The production of soap manufacturing is done by various processes. Different companies and manufacturers select different process for the production of soap. The first phase for the production of soap is selection of raw materials which is selected based on various factors such as cost, compatibility with other ingredients, safety for humans and environment, form of final product. There are four steps for the industrial soap production which includes:

1. Saponification
2. Removal of Glycerin
3. Purification of soap

4. Finishing

Although there are two methods for saponification here, we will briefly discuss the two different processes here. In first step, that is in saponification animal fat, coconut oil is mixed with Sodium Hydroxide (NaOH) then heated which produces salt of long chain carboxylic acid which is soap. In second step, glycerin is removed as it can be used in various cosmetics. Salt is added to the wetted soap to separate out into glycerin and soap which is precipitated in salty water as soap is not soluble in water whereas glycerin is. The softness of the soap is attained by the presence of remaining glycerin. In third step, remaining NaOH is neutralized with weak acid like citric acid and only one third of the water is left and rest is removed to have pure soap. Finally, the soap is mixed with dyes for colors, fragrance and preservatives and then shaping them into various shapes which is then packed and produced in the market for sale.

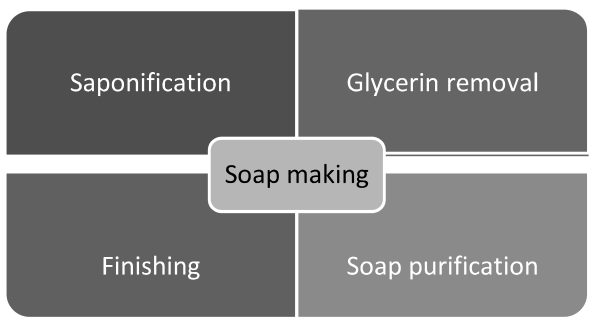

Figure 4: Steps involved in the formation of soap

Toilet soap are manufactured in the same way but only has less quantity of water and more fatty material than laundry soap. Toilet soaps are blended with preservatives before it is vacuum dried to remove unreacted caustic which is left in the soap also making it softer. Along with opacifier, perfumes and dyes are added to dried soap which is then evenly mixed [14].

Detergents

In place of fatty acids, synthetic surfactant is used for the production of soap. Detergents have soap in them however it functions as foam depressant. Powdered detergents are manufactured by various ways, like spray drying, agglomeration or combination of both.

In spray drying process, dry and liquid elements are mixed in cruncher to form a slurry or thick suspension. Then it is heated and pumped to the top. Then with high pressure it is sprayed through nozzles to form hollow granules as it dries. By the hot air current, droplets fall and are collected from bottom of spray tower. The granules are separated to gain standard size. As the granules dry, bleach and fragrance are added after cooling, bleach, enzymes and fragrance are added as they are sensitive to heat.

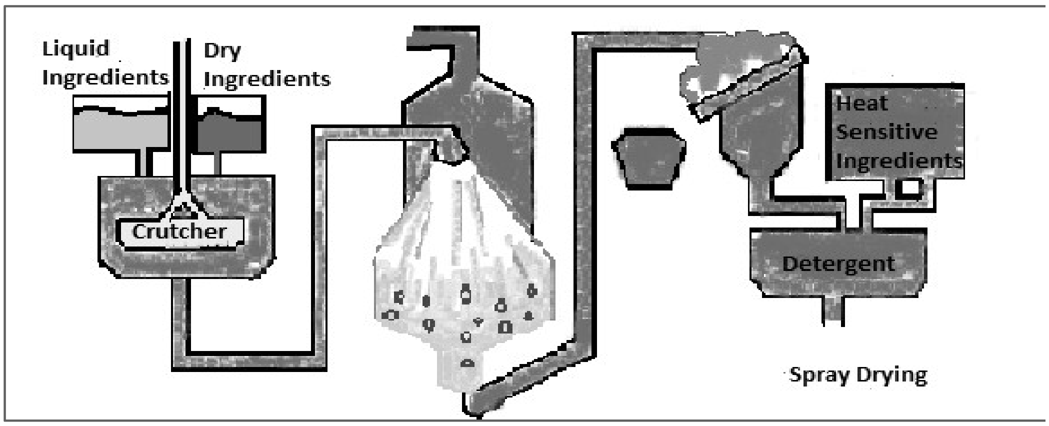

Figure 5: Diagram of spray drying

In agglomeration, raw materials are blended with liquid components. It is done with the help of machines such as liquid binder, rolling or shear mixing which produces larger and high-density particles. In dry mixing, raw materials are mixed and only little amount of liquid is added [15].

Ingredients of Soap

Soaps are made with many ingredients which have different purposes to serve for soap to act not only as a cleaning reagent but also for other purposes. The most ingredients which are present in the soap to function as a saponified oils are palm oil, tallow, stearic oil, palm kernel oil and olive oil. Along with oils, there is much presence of water. Soap also contains ingredients which serve as anti-acne compounds as well as moisturizing compounds. For anti-acne reagent benzoyl peroxide, sulfur and salicylic acid are present and for moisturizing agents it also has urea, leaf extract of aloe vera, propylene glycol and lactose. For lathering, Di-Sodium Cocoyl Glutamate, Sodium Lauryl Ether Sulphate, Cocoamidopropyl Betaine, TEA Oleate and Lauramine Oxide which act as a secondary surfactant. To hydrate skin, castor oil, silicone fluids, glycerin and

Glycerol monostearate. To resist cracking fatty acids of coconut is used. Titanium dioxide helps to bleach the skin. There is also presence of Tricloson, Trichlorocarbon which fights against pathological bacteria. Perfumes, vanilla are added for scent. To increase the viscosity, benzoic acid and PEG hydrated castor oil is combined. Hydroxyethane Diphosphonic acid and EDTA are present as chelating reagents. For colors, chromium hydroxide green, Dyestuff, Carbazole Violet and β-Carotene are there. Lastly, antioxidants in soap helps to prevent rancidity. [6]

Ingredient functions	Average value (%)	References
Saponified oils	47.5	[6]
Water	17.5	[6]
Anti-acne compounds	5.25	[6]
Moisturizing agent	5.05	[6]
Secondary surfactants	2.75	[6]
Emollienting agent	2	[6]
Crack resistance agent	2	[6]
Bleaching agent	1.05	[6]
Antibacterial agents	0.9	[6]
Fragrance	0.75	[6]
Thickening agent	0.55	[6]
Chelating agent	0.1025	[6]
Colorant	0.0505	[6]
Antioxidants	0.0075	[6]
Ph buffer	0.50	[6]

Table 1: Common ingredients of soap and its average amount that is present in the soap

Figure 6: Chart representing ingredients present in the soap

Ingredients of Detergents

For detergents, there are ingredients which are both in solid and liquid forms which have different roles to play for the detergent to perform various functions. In liquids there are five ingredients. First one is Linear alkylbenzene sulfonate (LAS) which is known to be the main active ingredient. It has strong cleaning power. To neutralize LAS, it is treated with Caustic Soda. For lathering either fatty alcohol ethoxylate or Coconut diethanolamide is added. Fluorescer emits blue light after absorbing UV light which causes aging cotton to appear white. Lastly, water serves as dissolver to dissolve various ingredients both solid and liquid and mix them better. For solids, Sodium Triphosphate (STP) is added as water softener and as pH buffer which helps to reduce alkalinity. Sodium sulphate is a freeflowing agent which also bulks the detergent. Another ingredient for foam formation is soap noodles which causes foam while rinsing. In some countries instead of STPs, Zeolites are used. It acts as water softener by absorbing elements such as Ca^{2+} and Mg^{2+} from hard water and also acts as granulating agent in concentrated detergents. To repel dirt particles which consists of positive charge, Sodium Carboxymethyl cellulose is used which helps to increase negative charge on cellulose fibres like cotton, rayon etc. [15]

Ingredients of Detergents	
Liquids	**Solids**
Linear alkylbenzene sulfonate (LAS)	Sodium triphosphate (STP)
Caustic Soda	Sodium sulphate
Fatty alcohol ethoxylate or coconut diethanolamide	Soap noodles
Fluorescer	Sodium carboxymethyl cellulose

Table 2: Ingredients of detergent

Problems

The maximum products which fall under the category of these cleaning reagents are harmful for the environment due to various reasons.

If we talk about the degreasers, for example TCE which was used in the early 1990s broadly for its ability to work effectively as degreasing agent. It also worked as dry-cleaning solvent in paints, painkillers and printing inks. But it got mixed with ground and surface waters when disposed by the industries as waste which gets contacted to us through ingestion, dermal absorption or inhalation causing alteration in protein’s normal function in the body. TCE is known to be carcinogenic for humans. Kerosene too is harmful for human body. It may cause irritation to skin, making skin red, sore and itchy when skin exposed to it [16].

In case of acids, acid cleaners must be used with precautions as some acids which are harsher and should not be left on surfaces as it can cause damage on the surfaces. Harsher acids are harmful reagents. It may cause accidental hazard if handled incautiously and for the environment if disposed carelessly.

In industries for cleaning the surfaces, stream of abrasive material is shot against the surface which is called as Sand-blasting or it is also identified as abrasive blasting. During this process the fine dust particles produced contributes to affect both the human and the environment by causing dust pollution [17].

Major problem arises from the soaps and detergents which are used on the daily basis by us especially after COVID. Around 0.4 to 9 ml hand wash is used by the people. But when certain amount of surfactants which are core ingredient in synthetic detergent in large amount causes damage when drained down to the water bodies and enters the soil changing its structure thus endangering plant's life [18],altering the pH level which should be 5-9 for the plants therefore threatens the soil's biological activity[19]and goes to groundwater or just in soil and sediment that is in the different sections of environment via sewage may directly or indirectly and changing the physicochemical properties of soil and surface waters and affecting the aquatic animals causing

1. Damages to fish gills.
2. Destroys the external mucus layers of fish which protects them from bacteria and parasites.
3. Lowers the surface tension which makes aquatic insects to float on surfaces of water.
4. Affects some insects living in water which is the food for fishes.[20]

Many surfactants present in the products formed conventionally, biodegrade slowly or into more toxic and bio accumulative chemicals hampering aquatic systems. Also, some constituents present for example alkylphenol ethoxylates which are known to function as endocrine disrupter which causes adverse effect to reproductive system of aquatic lives present in polluted water. [21]

Also, during COVID, the water used for washing hands after soap which is discharged into sewage carried the soap surfactants which create problems in wastewater treatment. If the water is released in the freshwater without any treatment then it would affect the humans who would consume water and also the environment.

> It also affects humans when the water is used for consumption from that particular water bodies by the formation of white foams in rivers caused by the phosphates which lessens water quality that can result in the reduction of oxygen dissolved in water and blockage of light leading to death of fishes and plants. [22]. The formation of soaps and detergents are from one or more petrochemicals. For detergents there is presence of Methanol, Ethylene, Toluene, Propylene which is considered to be non-biodegradable. Also, the cleansing agent in synthetic soaps is SLS which is Sodium Lauryl Sulfate. It also contains artificial scents and colorant which can possibly irritate the skin. [6]. It may also cause dryness to the skin especially in the face which would be problematic for the people living in dry areas and individuals with sensitive or dry skin [23].

There is also existence of phosphates in the detergents for its ability to increase efficiency of detergent and also has low cost whose role is to act as a nutrient that helps for the growth of the algae resulting in eutrophication [24]. This is life threating for the sea species especially corals and seaweeds. The impact on the sea plants due to eutrophication may affect sea animals which seek shelter in these plants, depend on plants for their food and use as their protection from other sea animals [25]. It also changes the pH of the water, salinity, temperature, turbidity. Although most surfactants can be degraded by microbes but some surfactants such as LAS (linear alkylbenzene sulphonates), DTDMAC, Alkylphenols cannot be removed. Alkylphenols are capable of inducing the production of Vitellogenin (at concentration of 5μg/L) in male fish [26].

The production of detergent powder may also contribute to the issues such as volatile organic emission from the spray drying tower and formation of dust during the process of transfer of the powdered detergent.

Also, the other chemicals which are used for cleaning are the chelating reagents which include Sodium salts of Ethylenediaminetetraacetic acid (EDTA-Na2 and EDTA-Na4). These are generally used to remove Copper and Bronze corrosion coatings. But these chelating reagents cannot be removed through water purification treatment and being non-biodegradable may result in affecting the environment [27].

Therefore, there is a dire need of compounds which are non-toxic, biodegradable and environmentally friendly having lower impact on the environment to replace these toxic and non-biodegradable components which are present in the cleaning agents that are used much frequently by the people for our planet, environment and also for well-being of the consumers and employees. It helps to decrease the pollutants which are toxic and harmful generated by the use of the synthetic products in the environment hence improving the air quality.

Synthetic soaps, detergents and other cleaning reagents carrying synthetic fragrances are toxic for humans if ingested and it is also harmful as 95% chemicals present in these fragrances are actually originated from petroleum which is non-renewable. These petroleum-based chemicals are harmful as it has potential to:

- Neurological disorders
- Cancers
- Failing of immune system
- Allergies
- Infertility
- Learning disabilities
- Alters hormones

Therefore, using green cleaning reagents helps to reduce the risk of neurological orders, cancers, allergies and much more. The usage of medicated soap is not so effective for prevention of diseases than regular soap. Such soap contains ingredients which have ability to cause hormonal problems. In case of green cleaning reagents such ingredients are absent which makes them safe to use. [26]. Also, Triclosan (TCC) and Triclocarban (TCS) which is present in antibacterial soap goes in the water it cannot be completely eliminated which may disturb the ecosystem and badly affect the aquatic lives. Wastewater treatment process is sabotaged by these antibacterial additives [29]. Under sunlight, TCS in water reacts forming chloroform which is possibly carcinogenic to humans [30].

Greener approach for Synthetic Cleaning Reagents

In the last few years, the demand for the cleaning reagents has been increased widely because of COVID-19. At present times consumers know the benefits of green products and also the harmful effects caused by the chemicals present in the synthetic cleaning products helps them to avoid the risks caused by these products. Also, many corporate initiatives are attentive towards the environmental issues such as KPMG's Global Green Initiative [31].

Instead of synthetic cleaning reagents we opt for green cleaning reagents which are non-toxic, biodegradable, generates less waste and which are formed using sustainable manufacturing processes. These cleaning reagents are conscious of the health of humans, well-being of environment and our planet. But the green products are still not effective in the market as some consumers are reluctant to buy environmentally friendly (EF) products as they believe it to be ineffective and also for its cost. Not every consumer is willing to buy premiere green products. Still consumer's perception may vary by changing barriers [32].

Although green products that look expensive but ultimately the product will be best and affordable and eventually realize how cheap they are. Another factor which makes consumers opt out for green products is its less effectiveness. But we need to think regarding well-being of the environment and recall the impacts caused by it.

We can use green alternatives in place of harmful ingredients that are used in the cleaning industry which are:

- Instead of colourants, Sodium sulphate, synthetic antimicrobial agents, Sodium silicate, Sodium hydroxide, preservatives, and non-natural perfumes we can use seeds of African copaiba balsam tree, common basil, shea tree, leaves and seeds of drumstick trees, and basil leaves. These are derived from renewable resources. It is also highly economical than the commercial soaps. It also helps to produce herbal medicated soaps which are biodegradable [33].

- Industrial antioxidants which are used in soaps can be replaced by Quinces and flakes of Cranberry fruit as these store antioxidant activity in them [34].
- Shea butter and Palm kernel oil can be used as a substitute of antibacterial agents like Triclosan (TCS), trichlorocarbanilide and chloroxylenol that are used in soaps. Neem oil, shea butter oil, green and betel plant can be used in place of trichlorocarbanilide which acts as an antimicrobial agent against microorganisms like B. subtilis and S. aureus. Green and betel plant also have moisture content for glycerol soap.

Acalypha indica can also substitute synthetic antimicrobial agents for having antifungal and antimicrobial activities [20, 35, 36, 37]. To replace synthetic fatty acids, avocado, aloe vera, basil, guava leaf, almond shells, orange peels, beef tallow, waste cooking oils, olive and rapeseed-palm fried oils, neem oil and fat and flesh that are obtained from the tannery industry can be used. Avocado also acts as a chemical emulsifier. It has excellent biochemical properties. Aloe vera, basil and guava leaves can be used for producing toilet soaps which are both economical and practical. It also has antioxidant values and is suitable for various types of skin. Hull of almonds and peels of orange fruit are low-priced, useful and produces remarkable green soap. It also promotes recycling with eco-friendly approach. Rendered beef fat and waste cooking oils lessens pollution, produces cost-effective eco-friendly toilet soaps. Olive oil and rapeseed-palm fried oils produces cost-efficient and natural sustainable soaps. These have green perspective and soap wastewater treatment becomes more controllable than used oil waste treatment. Neem oil is a low-cost source of fatty resources which can be used for toilet soap production. It can replace Isopropyl synthetic fatty acids. It is appropriate for allergic skin disease like acne, eczema and psoriasis. It can also replace Diethanolamine and Butylated hydroxytoluene. When fat and flesh which are from leather industry is used as fatty acids, it reduces the impact of leather waste and becomes a new resource for fat supply for the formation of soap by using waste of tannery industries [38, 39, 40, 41, 42, 43]. Sapogenin (Saponaria officinalis) are biodegradable, have low carbon and ecotoxicity footprints and have good economic efficiency. It can be used in place of chemical surfactants [44].

For fragrances we can use coconut oil, Oenothera biennis, palm fruit oil, pignut oil, olive oil or maize oil. These are eco-friendly and are harmless for the humans [45].

Instead of Butylated hydroxytoluene (BHT) and Butylated hydroxyanisole (BHA) we can opt of wild berry and Indian three-leaved yam. Wild berries help natural herbal soaps to have longer life. Indian three-leaved yamis is neutral in pH and acts as an antioxidant [35, 46].

Cysteine-octanoyl binds to the metal well and can form foam over wide range of pH, its bonds are so fragile that it breaks into cysteine and octanoic acid in the environment, does not add any hazardous waste and has acceptable biodegradability and biological degradation can substitute for Sodium Dodecyl Sulfate (SDS) and Sodium Lauryl Sulfate (SLS) which are present in the soap [47].

Biodegradable soaps can be used which are manufactured by the industries instead of synthetic soaps which are made from plasticizers, parabens, binders and preservatives which can be produced majorly via fermentation, give good performance in extreme conditions, has structural diversity and has selectivity [48].

Also, the herbal soaps which are plant- based renewable sources serves 17 sustainable development goals which are proposed for the betterment of the planet by UN as these soaps provide safe and high quality of water, has clean energy development and sustainble community development.[33]

Since the toxicity of synthetic antioxidant is gained so it needs to get replaced using additives from nature which are by-products of fruits and oil seeds,spices, vegetables, plant resources and culinary herbs which carriesgreat level of phenolics also other active ingredients. These are derived from agro-industry [35, 49].

Synthetic detergents can be replaced with safer natural detergents which are originated from coconut palm oil, enzyme and lipase which cleans protein stains. But some natural detergents may cause allergies, have low yields and high cost. We can use HNT (halloysite clay nanotube) which are non-toxic, multifunctional, green and cheap detergent. It can remove chili oil, tea, ink stains from textiles with much cleaning efficiency which is higher than 88% due to its higher adsorption ability, large aspect ratio and small size [50].

Homemade products like vinegar, lemon juice, coffee powder, salt, hot water can be used for cleaning purposes. It has less to no toxicity which makes it safe to use [24].

Chelating solutions mainly used for chemical cleaning such as Sodium salts of EDTA which is known to be non-biodegradable so we need to replace it. Dissolvine GL is known not only to be biodegradable but also cost effective. It is commercialized as green alternative to EDTA [51].

Although microbial cleaning has low efficiency but it is environmentally friendly. In this process, microorganisms are used to decompose impurities present on the surface mainly used for removal of oil and organic pollutants.

In MNBs (micro nano-bubbles) cleaning technology, large number of micros to nano sized bubbles are used to clean the work-piece. Here shock waves and liquid jets are produced from bubble rupture. It can be use in place of sand blasting process as it cleans gently which is absent in sand blasting. Large numbers of small impacts are applied on the surface of the object. The nanobubbles produce free radicals whose oxidation and disinfection increases cleaning process [52].

Ca- HDS-L is histidine-based additive. It is more effective as detergent.

dl- valine is also an ecofriendly detergent and also dispersant additive for the lubricants based on vegetable-oil when evaluated by blotters spot [53].

Phosphates can be replaced by zeolites and aluminosilicate having higher capacity of ion exchange and high porosity which helps to soften hard waters.

Non-ionic surfactants obtained when oil and bran of soy which is a natural polymer undergoes acid hydrolysis forms amino acids which when reacts with oil forming surfactant as a product [24].

Instead of hazardous surfactants, use of biosurfactants and plant surfactants will reduce the harmful effects on the nature. Biosurfactants are formed by many microorganisms and plants. They can act as emulsifiers, have foaming properties. Some plants secrete several secondary metabolites which carry many surfactant properties -these are plant-based surfactants. It can be found in different parts of plants [54].

Cleaning action of some green compounds which can be used as cleaning reagents:

Zeolites-

In place of phosphate additives zeolites can be used. Zeolite which is commonly used for cleaning in detergents is Sodium zeolite- A. The structure of zeolites is formed by the linkage of AlO_4 units at the corners of tetrahedral SiO_4 so that pores are formed within its framework. These pores help to adsorb ions which are smaller or equal in size and avoiding the larger ones. Sodium in Sodium zeolite-A from its framework gets removed in hard water by the ions which are present that are Ca^{2+} and Mg^{2+}. This action results in softening the water that is removing the ions from it [55].

Biosurfactants -

Biosurfactants have ability to work like chemical surfactants. Between two phases, the surface and interfacial surface are reduced by the biosurfactants. For example: - Surfactin, which can act as emulsifier. It has two parts where one part is water loving(hydrophilic) and other part is water repulsive that is (hydrophobic) thus showing amphiphilic surface activity. This helps them to combine the interface of two liquids which can be either immiscible or poorly miscible thereby reducing interfacial tension of the two liquids or different material phases thus giving it its emulsifying property [56].

Plant-based surfactants-

Now a days, soap bar contains sodium salts of palm kernel acid which is also known as sodium palm kernelate which is made when fatty acids of palm kernel reacts with sodium hydroxide. It can replace the harsh surfactants as it shows surfactant properties which are used in soaps and can also act as emulsifying agent [57].

Dissolvine GL-

Dissolvine GL is produced from naturally occurring amino acid i.e. monosodium L-glutamic acid. It can act as a chelating agent. It can hold the ions (Ca2+ and Mg2+) which are present in hard water very strongly than the other chelating agents, even at high temperatures. Thus, eliminating the ions that interferes with the cleansing effect of soaps and detergents thereby softening the water.[58]

MNBs-

MNBs stands for micro nano bubbles having less than 100μm diameter and which can be produced with various methods like rapid gas release, electrolysis, external electric field,microporous aeration, ultrasonic cavitation, and mechanical shear. MNBs are generally formed using two methods which are microporous aeration and mechanical shear.

MNBs have physical characteristics like in bubble breakup, jet impingement occurs. This jet impingement helps detaches pollutants from solid surfaces which due to strong grip will be difficult to remove. Also, the large surface area of those small bubbles helps the linkage of pollutants with bubbles. The low density of the MNBs from the liquid helps the oil to float on the surface which is flotation effect. It also tends to combine with hydrophobic contaminants in water which can adsorb oil stains from the surfaces of solid by the bubbles.

Also, in MNBs, the active oxygen containing free radicals purifies the surfaces and can oxidize and eliminate organic matter. [52]

Sapogenin (Saponaria officinalis L.)-

The common name for Saponaria officinalis L. is soapwort. For cleaning purposes, its roots and leaves are used. Saponins are amphiphilic glycosides which includes hydrophilic glycone moieties attached with hydrophobic aglycones moieties which are called sapogenins.A saponin molecule contains a hydrophobic part which may be terpenoid or water insoluble steroid and hydrophilic part which has water soluble head thus it can be said to be non-ionic surfactants. Due to presence of natural surfactants, they can exhibit foaming property. As stable foam forms so the addition of any stabilizer is not needed. Saponins are also known to be good emulsifiers. Also, with their hydrophobic core, they have ability to dissolve organic non-polar compounds. [59]

Cysteine-octanoyl –

L-cysteine is a semi-essential amino acid that is biosyntheticmainly in hair, fingernails and skin. It exhibits high efficiency in absorbing metal ions from wastewater because of the functional groups active on its surface. [60]

HNT –

HNT stands for Halloysite nanotubes which has molecular formula of $Al2(Si2O5)(OH)4 \cdot nH2O$. It has tube like structure with size of 0.02-30μm where aluminum oxide octahedron is on the inside having diameter of 10-30nm and outside of the tube is present with silicon oxide tetrahedrons having diameter of 30-70nm. Due to its structure, it shows decrease in surface tension than SDS, DTAB and Triton X-100 and rise in Pickering emulsion due to its small size that aids to clean tints on different substrates by getting absorbed at oil-water interfaces and breaks the linkage of oil with the substrates by washing movement. After oil discharges from the surface, to stabilize the oil droplets, HNT as stabilizer is tightly positioned at the oil-water interface thereby making oil droplets unable to reattach to the surface hence giving removing it for good. [61]

Instead of	**Use**	**References**
Colourants, sodium sulphate, synthetic antimicrobial agents, sodium silicate,Sodium hydroxide,	Seeds of African copaiba balsam tree,Common basil,shea tree,leaves and seeds of drumstick	**[33]**

Instead of	**Use**	**References**
preservatives, and artificial perfumes	trees, and basilleaves.	
Industrial antioxidants	Quinces and cranberry fruit flakes	[34]
Antibacterial agents like Triclosan (TCS), trichlorocarbanilide and chloroxylenol	Palm kernel oil and shea butter, neem oil, shea butter oil, green and betel plant	**[20], [35] – [37]**
Synthetic fatty acids	Avocado, aloe vera, basil, guava leaf, almond shells, peels of orange fruit, rendered beef fat, waste cooking oils, olive and rapeseed-palm fried oils, neem oil and fat and flesh which are extracted from the tannery industry	**[38],[39], [40]-[43]**
Chemical surfactants	Sapogenin (*Saponaria officinalis*)	**[44]**
Artificial fragrances	Coconut oil, *Oenothera biennis*, palm fruit oil, pignut oil, olive oil or maize oil	**[45]**
Butylated hydroxytoluene (BHT) and Butylated hydroxyanisole (BHA)	Wild berry and Indian three-leaved yam	**[35]**
Antioxidant	Indian three-leaved yam	**[46]**

Instead of	Use	References
Sodium dodecyl sulfate (SDS) and Sodium lauryl sulfate (SLS)	Cysteine-octanoyl	**[47]**
Synthetic soaps	Biodegradable soaps, herbal soaps	**[48],[33]**
Synthetic antioxidant	Natural additives	**[35],[49]**
Synthetic detergents	HNT, dl valine	**[50]**
Toxic cleaning agent	Homemade cleaning reagents	**[24]**
EDTA	Dissolvine GL	**[51]**
Sand -blasting	MNB (micro nano bubbles)	**[52]**
Detergent additive	Ca-HDS-L	**[53]**
Phosphates	Zeolites	**[24]**
Surfactants	Non-ionic surfactants, biosurfactants, plant-based surfactants	**[24]**

Table3: Representation of the green alternatives for the synthetic products

Conclusion

The practice of cleaning reagents especially soaps and detergents has been for ages. From the mixture of wood ash and animal fat, it slowly developed decades after decades to work effectively. In the current day, there are many types of soaps and detergents which are manufactured along with other cleaning reagents. The use of soaps and detergents are very much regular in every household especially the usage of these cleaning reagents was accelerated after COVID-19 hit the world. But such practice also impacted the environment badly because of the presence of harmful, toxic, non-biodegradable chemicals which are the present as the components in the cleaning reagents. These also affect the soil's pH thus hampering the plants.

These components also have the ability to affect the human health and also the lives in the aquatic system due to the disposal of the wastewater in the rivers. Like the presence of phosphate in detergents which causes eutrophication disturbing the aquatic plants and animal.Moreover, the presence of toxic surfactants in the water also disturbs the aquatic systems which can be also harmful when the water containing these toxic chemicals is consumed by the humans. Also, the presence of chemical fragrances which are also harmful. There are many other components which have an ability to affect the ecosystem. Consequently, the necessity to change these toxic chemicals with the biodegradable, less waste generating and sustainable becomes a must. There are many eco-friendly, non-toxic, natural materials which can become substitute for these synthetic materials. Like phosphates, which can be replaced by the use of zeolites. Similarly, the use of biosurfactants or plant-based surfactants instead of synthetic surfactants. Thus, using the green products or the products which are non-toxic will be beneficial for both environment and humans and which would help to overcome the impacts that are caused by the toxic, non-biodegradable ingredients that are present in the cleaning agents.

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