IJARSCT

International Journal of Advanced Research in Science, Communication and Technology

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

ISSN: 2581-9429 Volume 5, Issue 10, March 2025 Impact Factor: 7.67

A Comprehensive Study on Extraction of Limonene from Orange Peels

Neelam Nisar Dhansay and Pankaj Gaikwad

D.G. Tatkare Mahavidyalay, Mangaon- Raigad, Maharashtra

Abstract: *Orange peel wastes, with an estimated global annual production of 25 million tonnes, are problematic to dispose of but can be used to obtain a range of valuable products, among them the main constituent of orange essential oil, D-limonene (DL). This review aims to layout recent advances in the field of DL extraction and purification. Besides substitution of the conventional solvent hexane with certain bio-based solvents, a range of techniques are presented. These include enhanced solvent extraction processes through temperature and pressure intensification or ultrasound, improved distillation most commonly using different microwave-based techniques but also enzymes, and supercritical CO2 extraction. Even though purification has been found to be the most energy- intensive and environmentally impacting step, most studies did not improve on existing centrifugation, decantation, or fractional distillation methods. Chromatography has been proven effective at obtaining high DL purities; however, it still has to be improved because of its high costs and low productivity.*

D-Limonene is a compound that can be acquired from the rinds of the citrus family like oranges, limes, and mandarins. it is quite possibly the most well-known terpene present in nature. It has a few applications and a wide scope of advantages. Numerous medical service suppliers have supported the possible advantages of D-limonene guaranteeing that it can forestall or treat some ailments, for example, Bronchitis, Cancer, Diabetes, Gall stones, etc. It is likewise utilized in enterprises to make hand sanitizers, fragrances, plant pesticides, and synthetic solvents..

Keywords: D-Limonene, Orange Peels, Orange Essentiol Oil, Simple Fractional Distillation, Solvent Hexane, Extraction.

I. INTRODUCTION

D-Limonene is an essential oil that is available in high concentrations in the peels of citrus fruits. Which has several uses and applications in many disciplines including cosmetics, pharmaceuticals, and cleaning solutions. And it can also be used as a Biofuel because of its flammability [1,7]. Extraction of this highly useful essential oil from the peels of citrus fruits can be done in many methods such as (1) Cold Pressing (2) Solvent Extraction (3) Simple Distillation. Super Critical CO2 extraction [2,3]. In the current investigation, we used Simple Distillation set for the process of extraction of D-Limonene using orange peels [11,14]. Limonene is a popular additive in foods, cosmetics, cleaning products, and natural insect repellants[13]. For example, it's used in foods like sodas, desserts, and candies to provide a lemony flavor. Due to its strong aroma, limonene is utilized as a botanical insecticide [6,9]. It's an active ingredient in multiple pesticide products. Other household products containing this compound include soaps, shampoos, lotions, perfumes, laundry detergents, and air fresheners [10]. Limonene has been studied for its potential anti inflammatory, antioxidant, anticancer, and heart-disease-fighting properties. One line that fits best to our motivation in initiating this project is BRINGING THE BEST OUT OF WASTE". Every year, a whopping 3.8 million tons of orange peels are dumped as waste. D-Limonene is an essential oil that can be extracted from orange peel wastes, which costs around Rs.500/- to Rs.700/- per ounce in the current market. Extracting D-Limonene from such discarded orange peels gives us two benefits which are extracting essential oil and reducing the orange peel waste. [12,15].

During the processing of citrus fruits, approximately 50% of the fruit weight is wasted as peels and pulp, which includes seeds and membranes (Santiago et al., 2020), as well as the inner peel, called albedo comprising about 17% of the total fruit weight, and the outer peel, or flavedo, comprising 10% of total fruit weight (Zema et al., 2018), as shown in Fig. 1. About 30% of all citrus production goes to processing, main the production of juice. Oranges, mostly referring to the sweet orange Citrus sinensis but at times also to the bitter orange Citrus aurantium, are the most commonly consumed of all citrus fruits (Izquierdo and Sendra, 2003) at an estimated production of 72 million tonnes. Thus, orange peel made up a significant fraction of the approximately 25 million tonnes of citrus wastes generated globally in 2016 (Zema et al., 2018). In the European Union (EU) alone, the production of this waste stream in 2013 exceeded 10 million tonnes.

Due to its low pH and high water and organic matter contents, citrus wastes are legally not disposable in landfills in the EU (EU Waste Framework Directive, 2008), and their use as animal feed, though nutritious, can cause digestive diseases in livestock when introduced in larger quantities (Martín et al., 2010). Some established waste management practices include anaerobic digestion, composting, and incineration (Flotats et al., 2015). However, great potentials lay in the utilisation of orange peel wastes in bio-refineries as feedstock for fermentation and source of carbohydrate polymers, enzymes (Ozturk et al., 2019, Panić et al., 2021), and various bioactive compounds with pharmaceutical applications (Montero-Calderon et al., 2019).

D-Limonene from Orange Peel :-

Limonene, one of the most abundant naturally occurring components of cannabis essential oils, is a plant product of terpenes. It is present in concentrations as high as 16% of essential oil fractions. Limonene is a clear, colourless hydrocarbon classified as a cyclic monoterpene, and is the major component in oil of citrus fruit peels most widely distributed in nature. It occurs naturally in orange peels, lemon, dill, mint, cumin and neroli. Limonene occurs in two optically active forms, (S–(–)–limonene and R–(+)-limonene). It also has two isomeric forms (D–isomer and L–isomer). D–limonene, a monocyclic terpene, occurs more commonly in nature. It is the fragrance of oranges and is used as a flavouring agent in food manufacturing (Ludwiczuk et al. 2017). Studies have shown that D–limonene is toxic to animals such as dogs (680 g/kg dosage) and cats. Also it has insecticidal properties and acts primarily as a desiccant for all life stages of insects such as flea, ticks, etc. Therefore, it is a component of some products made from citrus oils such as soaps, shampoos, cleansers, solvents, fragrances, and insecticides (Plumlee 2013). The less common L-isomer is found in mint oils and has a piney, turpentinelike odour. Anti-tumour activities of the compound in several animal tumour models and in vitro experiments have been reported (Amanzadeh et al. 2006, Barceloux 2008).

II. LITERATURE REVIEW

M. Boluda-Aguilar et al. Production of bioethanol by fermentation of lemon (Citrus limon L.) peel wastes pretreated with steam explosion, Ind. Crops Prod. (2013). The application of steam explosion and enzymatic hydrolysis pretreatments on lemon (Citrus limon L.) citrus peel wastes was studied to obtain bioethanol, galacturonic acid and other co- products, such as D-limonene and citrus pulp pellets. Steam explosion pretreatment and recovery of lemon citrus essential oils was carried out at pilot plant scale. The effect of steam explosion on lignocellulosic composition of lemon peel wastes was studied by thermogravimetric analysis. The antimicrobial activity of lemon essential oil on Saccharomyces cerevisiae and its influence on ethanol production during fermentation were also studied. The steam-exploded lemon peel wastes were processed by sequential and simultaneous hydrolysis and fermentation. Concentrations of sugars, galacturonic acid and ethanol were analyzed to measure the efficiency of these processes. Significant antimicrobial activity of lemon essential oils has been observed on S. cerevisiae at concentrations above 0.025%. The steam explosion pretreatment has shown an interesting effect on lemon peel wastes processing for obtaining ethanol and galacturonic acid. This pretreatment reduces the residual content of essential oils below 0.025% and significantly decreases the hydrolytic enzyme requirements. Ethanol production in excess of 60 L/1000 kg fresh lemon peel biomass can be obtained.

M. Boukroufa et al. Bio-refinery of orange peels waste: a new concept based on integrated green and solvent free extraction processes using ultrasound and microwave techniques to obtain essential oil, polyphenols and pectin, Ultrason. Sonochem. (2015). In this study, extraction of essential oil, polyphenols and pectin from orange peel has been optimized using microwave and ultrasound technology without adding any solvent but only "in situ" water which was recycled and used as solvent. The essential oil extraction performed by Microwave Hydrodiffusion and Gravity (MHG) was optimized and compared to steam distillation extraction (SD). No significant changes in yield were noticed: 4.22 ±

0.03% and 4.16 ± 0.05% for MHG and SD, respectively. After extraction of essential oil, residual water of plant obtained after MHG extraction was used as solvent for polyphenols and pectin extraction from MHG residues. Polyphenols extraction was performed by ultrasound-assisted extraction (UAE) and conventional extraction (CE). Response surface methodology (RSM) using central composite designs (CCD) approach was launched to investigate the influence of process variables on the ultrasound-assisted extraction (UAE). The statistical analysis revealed that the optimized conditions of ultrasound power and temperature were 0.956 W/cm2 and 59.83 °C giving a polyphenol yield of 50.02 mg GA/100 g dm. Compared with the conventional extraction (CE), the UAE gave an increase of 30% in TPC yield. Pectin was extracted by conventional and microwave assisted extraction. This technique gives a maximal yield of 24.2% for microwave power of 500 W in only 3 min whereas conventional extraction gives 18.32% in 120 min. Combination of microwave, ultrasound and the recycled “in situ” water of citrus peels allow us to obtain high added values compounds in shorter time and managed to make a closed loop using only natural resources provided by the plant which makes the whole process intensified in term of time and energy saving, cleanliness and reduced waste water.

J. Bustamante et al. Microwave assisted hydro-distillation of essential oils from wet citrus peel waste, J. Clean. Prod. (2016). Over 30% of the total citrus fruits grown all over the World are processed, generating large quantities of peel waste from which essential citrus oils are often extracted by traditional methods demanding high energy costs, long extraction times and additional reagents. In this research an alternative technique based on microwave- assisted hydro-distillation (MAHD) has been studied to successfully extract the essential oil present in wet citrus peel waste whilst reducing costs, avoiding the use of additives and improving the effectiveness of the process. To achieve this goal factors affecting the scalability of the process to develop a new bio-refinery model to be used at industrial scale were considered. Optimal conditions for the essential oil MAHD involved the irradiation of a waste orange peel:water mixture (1:1.5) over two subsequent steps using different irradiation powers for a total extraction time of 20 min (keeping a constant pressure of 300 mbar through all the process). The essential oil yield obtained in Navel Navelate oranges using MAHD accounted for 1.8± 0.1% (dry basis; n = 3) and was comparable to that obtained by conventional hydro- distillation (1.7± 0.1%; dry basis; n = 3). The applicability of the suggested methodology was successfully tested in other varieties of orange and citrus fruits leading to the potential to apply MAHD of essential oils from other waste feedstocks and offering an attractive process for future extraction processes at industrial scale.

Y. Dai et al. Natural deep eutectic solvents providing enhanced stability of natural colorants from safflower (Carthamus tinctorius) Food Chem. (2014). A certain combination of natural products in the solid state becomes liquid, so called natural deep eutectic solvents (NADES). Recently, they have been considered promising new green solvents for foods, cosmetics and pharmaceuticals due to their unique solvent power which can dissolve many non-water-soluble compounds and their low toxicity. However, in addition to the features as solvents, the stabilisation ability of NADES for compounds is important for their further applications. In the study, the stability analysis demonstrates that natural pigments from safflower are more stable in sugar-based NADES than in water or 40% ethanol solution. Notably, the stabilisation capacity of NADES can be adjusted by reducing water content with increasing viscosity. The strong stabilisation ability is due to the formation of strong hydrogen bonding interactions between solutes and NADES molecules. The stabilising ability of NADES for phenolic compounds shows great promise for their applications in food, cosmetic and pharmaceutical industries.

M. Panić et al. Enabling technologies for the extraction of grape-pomace anthocyanins using natural deep eutectic solvents in up-to-half-litre batches extraction of grape-pomace anthocyanins using NADES Food Chem. (2019). Bioactive compounds should be extracted using alternative solvents and enabling technologies, in accordance with green extraction principles. The aim of this study is to develop an eco-friendly extraction method for grape-pomace anthocyanins on a larger scale. From a preliminary screening of 8 different natural deep eutectic solvents (NADES), a combination of choline chloride:citric acid was selected because of its price, physicochemical properties, and anthocyanin recovery and stability. The effects of multimode-microwave (MW), and low- frequency-ultrasound (US) irradiation (used alone or simultaneously), as well as that of process parameters on extraction efficiency have been investigated in order to maximise anthocyanin extraction yield. The best conditions were found to be: simultaneous

IJARSCT
International Journal of Advanced Research in Science, Communication and Technology
International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal
ISSN: 2581-9429
Volume 5, Issue 10, March 2025
Impact Factor: 7.67

ultrasound/microwave-assisted extraction (UMAE) (MW power at 300 W, US power 50 W), for 10 min with 30% (v/v) of water.

B. Ruiz et al. Effect of limonene on batch anaerobic digestion of citrus peel waste, Biochem. Eng. J.(2016). The objective of this study was to analyze the anaerobic digestion process inhibition by limonene, the main component of citrus essential oils (CEO) present in citrus peel. The biochemical methane potential (BMP) values of the citrus waste tested (orange peel, mandarin peel, mandarin pulp and rotten fruit) were 354–398 LCH4 kgVS−1. Grinding the orange peel (2.5 glimonene L−1) did not influence the BMP values, but slowed the kinetics, due to the increased availability of CEO caused by the grinding. The effect of (R)-limonene (0–3000 mg L−1) on the batch anaerobic digestion of microcrystalline cellulose was also assessed. The half maximal inhibitory concentration, IC50, was 423 mg kg−1 in an initial run and 669 mg kg−1 in a second run of batch experiments. The methane course and IC50 values indicate that there are reversible inhibition and biomass activity recovery during the anaerobic digestion process, despite the non-reversible antimicrobial mechanism described in the literature for limonene to date.

N. Sahraoui et al. Valorization of citrus by-products using microwave steam distillation (MSD), Innov. Food Sci. Emerg. Technol. (2011). A microwave steam distillation (MSD) of essential oils from fresh citrus by-products (orange peels) was studied. The effectiveness of this innovative method in extraction of citrus essential oils have been evaluated and compared to conventional steam distillation. MSD offers important advantages like shorter extraction time (6 min), cleaner features and provides an essential oil with better sensory properties (better reproduction of natural fresh fruit aroma of the citrus essential oil) at optimized power (500 W). Results from chemical and cytological approaches confirm the effectiveness of this new technique, that allows substantial savings in terms of time and energy.

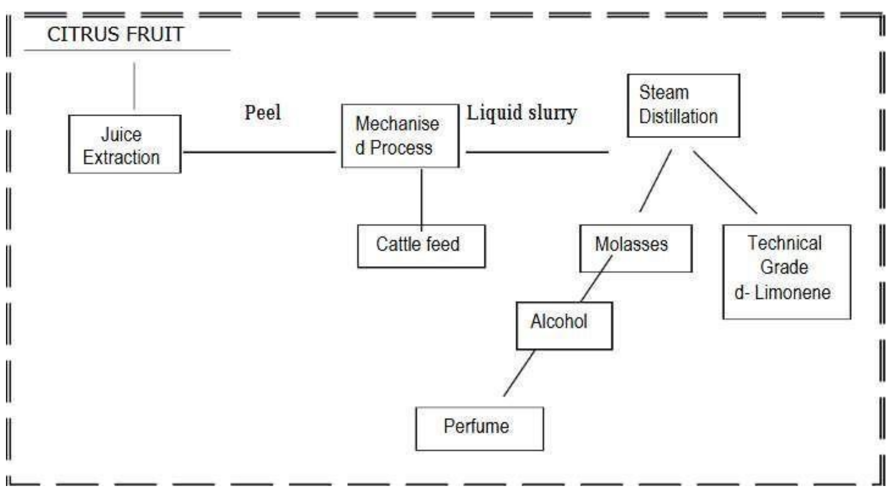

Figure:- Limonene extraction process.

Nutritional Values/100g:- Carbonhydrate9.0g,Dietary fibre2.3g, Sugars 2.5g, Fat 0.3g,Protein 1.1g,Water 89g, Vitamin C 53mg (88%), Citric Acid 5g. (Calomme et al.,1996).

Packaging and Shelf Life of D-Limonene:- Oxidation may occur between the time the oil is extracted and the time it is sealed into a container. So it must be kept in an airtight container. It must also be kept from contamination by inferior oil (deteriorated oil) or substance that might increase the rate of deterioration. The shelf life of lemon oil is only 8 – 10 months, if it is to be used in aromatherapy, but can still be used in fragrance therapies after this time, such as vapour therapy.

D-Limonene:- Limonene recovered from orange peel from the conversion of press liquor to molasses, d-limonene is used for making everything from adhesive to a solvent used by the electronic industry as a replacement of ozone depletion chlorofluorocarbons.Limonene is a hydrocarbon classed as a terpene, it is a clear coloured liquid at a room temperature with a strong smell of orange. It takes its name from lemon, like other citrus fruits, contains a considerable amount of this chemical compound responsive for the smell.(Stromvall, 1992: Rimpler,1999).

Physical Properties:- Limonene is colourless liquid oil at room temperature with a characteristic odour. It is insoluble in water but soluble in alcohol and ether. It has boiling point of 74OC.

Chemical Composition:- The main chemical compositions of lemon oil are a-pinene, camphene, b-pinene, sabinene, a-terpene, linalool, b-bisabolene, limonene, trans-a-bergamotene, nerol and neral. It belongs to the family (chemically) of cycloalkene called terpenes. Its IUPAC name is 4-isopropeny–1–methylcyclohexane. It has an aldehyde content between 0.13% - 1.50% (karbery; et al. 1992).

Therapeutic Properties:- The therapeutic properties of lemon oil are anti-anaemic, antimicrobial, anti-rheumatic, anti-sclerotic, antiseptic,. It also serves has bactericidal, carminative, cicatrizant, depurative, diaphoretic, diuretic, febrifuge, haemostatic, hypotensive, insecticidal, rubefacient, tonic and vermifuge.

Other Uses of Essential Oil:- Aromatherapy, Wound and Sores, Douching,Foots,Cataract,Cosmetics, Stimulating, anti-anaemic, antimicrobial, ant-rheumatic, catarrh, cold, bronchitis, throat infection, mouth ulcers, spots and varicose, Essences and Aromas, Cold Pressed Oil. (Opdyke,1978).

III. METHODOLOGY

The methodology for extracting limonene from orange peels typically involves either steam distillation, cold pressing, or solvent extraction. Below is a detailed methodology for extracting limonene using steam distillation, which is a common and efficient method.

Materials Needed:

- Fresh orange peels (preferably from ripe oranges)
- Distillation apparatus (including a distillation flask, condenser, and receiving flask)
- Water
- Heat source (e.g., electric heater or Bunsen burner)
- Separatory funnel (for oil-water separation)
- Ice (for cooling)
- pH paper (optional, for quality control)

Procedure and Steps in Steam Distillation for Limonene Extraction:

1. Preparation of Orange Peels:

- Cleaning: Wash the orange peels thoroughly to remove any dirt, pesticides, or other impurities.
- Peeling: Peel the oranges, ensuring that the peels are free from the bitter white pith as much as possible. You can use a knife or peeler to do this.
- Chopping: Cut the peels into smaller pieces or shred them to increase the surface area for better extraction.

2. Setting Up the Distillation Apparatus:

- Distillation Flask: Place the chopped orange peels in a distillation flask.
- Water: Add enough distilled water to the flask to submerge the peels. This water will help generate steam for the distillation process.
- Condenser Setup: Connect the distillation flask to a condenser. Ensure the condenser is properly connected to a receiving flask where the distillate will be collected.
- Coolant: Ensure that water flows through the condenser to keep the vapor cool and enable condensation into liquid form. Use a constant flow of cold water for cooling.

3. Steam Distillation Process:

- Heating: Heat the water in the distillation flask. As the water boils, steam will pass through the orange peels, carrying the essential oil (limonene) and other volatile compounds.
- Condensation: The steam and vapor mixture will rise through the condenser. The condenser will cool the mixture, causing the steam to condense back into liquid form.

• Collection: The liquid (a mixture of water and limonene) will flow into the receiving flask.

4. Separation of Limonene from the Water:

• Separation: After distillation, you will have two phases in the receiving flask: a water layer (hydrosol) and the essential oil layer (limonene). Limonene, being less dense than water, will float on top.

• Decantation: Carefully separate the two layers. The essential oil (limonene) can be separated by decantation or using a separatory funnel.

5. Purification of Limonene:

• Drying: If any water remains in the essential oil, it can be dried using anhydrous sodium sulfate to absorb the moisture.

• Filtration: The oil can be filtered to remove any remaining solids.

• Storage: Store the pure limonene in airtight containers, away from direct sunlight to preserve its quality and prevent oxidation.

6. Optional Quality Control:

• Purity Check: You can check the purity of the extracted limonene using techniques like gas chromatography (GC) or by its characteristic odor (fruity citrus aroma).

• pH Test: In some cases, checking the pH of the hydrosol or the distillate can help ensure proper extraction conditions, as limonene is acidic.

IV. CONCLUSION

The extraction of limonene from orange peels provides a valuable method for obtaining a natural, versatile compound with wide applications in industries such as pharmaceuticals, food and beverages, cleaning products, and cosmetics. In this study, steam distillation was utilized as the primary method for extracting limonene, offering a simple, efficient, and cost-effective means of obtaining this essential oil. The results indicated that steam distillation yielded a modest quantity of limonene from orange peels, with a purity that can be enhanced through optimization of extraction parameters such as temperature, time, and pressure. While the yield in this experiment was relatively low, it is essential to recognize that factors like the quality of the orange peels, the extraction method, and the scale of operation can significantly influence the efficiency of the process.

The process of limonene extraction not only presents an opportunity to recycle agricultural waste but also aligns with growing trends toward sustainable practices in industrial processes. As limonene is a renewable resource, the extraction process offers an environmentally friendly alternative to synthetic chemicals used in various products. Overall, the extraction of limonene from orange peels shows promise for both small-scale and large-scale applications, particularly in the context of sustainable practices. Future research and technological advancements, such as the optimization of extraction techniques and scaling up to industrial levels, will further enhance the feasibility and profitability of limonene extraction. Furthermore, exploring alternative applications and improving the yield of limonene will open new avenues for its use across a wide range of industries, making it an essential compound in the transition toward greener and more sustainable chemical processes.

V. ACKNOWLEDGEMENT

I would like to express my heartfelt gratitude to my advisor, Asst.Prof Pankaj Gaikwad for their invaluable guidance, support, and encouragement throughout the research process. I am also deeply thankful to Head of chemistry Department Asst. Prof. Mehreen Dawre, for their leadership and constant encouragement. My sincere thanks to Dr. B. M. Khamkar, Principal of D.G.Tatkare Mahavidyalay, for providing the necessary resources and fostering an environment conducive to academic growth. Finally, I am deeply grateful to my family and friends for their unwavering support and encouragement throughout this journey.

IJARSCT
International Journal of Advanced Research in Science, Communication and Technology
International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal
ISSN: 2581-9429 Volume 5, Issue 10, March 2025 Impact Factor: 7.67

REFERENCES

[1]. M. Boluda-Aguilar et al. Production of bioethanol by fermentation of lemon (Citrus limon L.) peel wastes pretreated with steam explosion Ind. Crops Prod. (2013)

[2]. M. Boukroufa et al. Bio-refinery of orange peels waste: a new concept based on integrated green and solvent free extraction processes using ultrasound and microwave techniques to obtain essential oil, polyphenols and pectin Ultrason. Sonochem. (2015)

[3]. J. Bustamante et al. Microwave assisted hydro-distillation of essential oils from wet citrus peel waste J. Clean. Prod. (2016)

[4]. Y. Dai et al. Natural deep eutectic solvents providing enhanced stability of natural colorants from safflower (Carthamus tinctorius) Food Chem. (2014)

[5]. M.A. Martín et al. Biomethanization of orange peel waste Bioresour. Technol. (2010)

[6]. M. Panić et al. Enabling technologies for the extraction of grape-pomace anthocyanins using natural deep eutectic solvents in up-to-half-litre batches extraction of grape-pomace anthocyanins using NADES Food Chem. (2019)

[7]. B. Ruiz et al. Effect of limonene on batch anaerobic digestion of citrus peel waste Biochem. Eng. J. (2016)

[8]. N. Sahraoui et al. Valorization of citrus by-products using microwave steam distillation (MSD) Innov. Food Sci. Emerg. Technol. (2011)

[9]. M.R. Wilkins et al. Hydrolysis of grapefruit peel waste with cellulase and pectinase enzymes Bioresour. Technol. (2007)

[10]. S. Yasumoto et al. Supercritical CO2-mediated countercurrent separation of essential oil and seed oil J. Supercrit. Fluids (2015)

[11]. Z. Zeković et al. Coriander seeds processing: sequential extraction of non-polar and polar fractions using supercritical carbon dioxide extraction and ultrasound-assisted extraction Food Bioprod. Process. (2015)

[12]. Y. Amanzadeh et al. New elaborated technique for isolation and purification of limonene from orange oil Iran. J. Pharm. Sci. Iran. Assoc. Pharm. Sci. (2006)

[13]. A. Arce et al. Citrus essential oil deterpenation by liquid-liquid extraction Can. J. Chem. Eng. (2005)

[14]. T.M. Attard et al. Microwave assisted extraction as an important technology for valorising orange waste New J. Chem. (2014)

[15]. A. Atti-Santos et al. Extraction of essential oils from lime (Citrus latifolia Tanaka) by hydrodistillation and supercritical carbon dioxide Braz. Arch. Biol. Technol. (2005)