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A Review of Green Technologies for the Extraction of Vanillin from *Vanilla planifolia* Leaves: Advantages and Limitations

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Vanilla is the most popular flavour in the world, especially in the food industry. Vanillin is obtained from the '*Vanilla planifolia'* orchid plant. Since non-synthetic vanilla is more expensive than the synthetic alternative, the availability of fake vanilla extracts has increased in the market. Green technology is an alternative method to produce vanillin from vanilla pods and leaves with minimal energy consumption. In this paper, several non-conventional green methods to extract vanillin are reviewed, such as Microwave-Assisted Extraction (MAE), Microwave Pre-treatment (MW), Ultrasound Technology and Subcritical Water Extraction (SWE), and the advantages and limitations of each technique are discussed. Since these methods have some limitations, the green catalyst oxidation system is introduced as a safer method to treat the leaves to obtain a higher purity and better quality product. This new class of catalysts can destroy some of the worst pollutants before they get into the environment. 'Green catalysts' (Fe-TAML/H2O2) are used to recover natural compounds as an alternative to conventional methods and can prevent the formation of hazardous substances and clean-up steps. This review investigates various methods for recovering vanillin from the leaves of *Vanilla planifolia* through sustainable green technology using the green catalyst as an oxidation system. Overall, MAE was found to be the best method for extracting vanillin from *Vanilla planifolia*.

Key words: Green technology; *Vanilla planifolia*; microwave-assisted extraction; microwave pre-treatment; ultrasound-assisted extraction; Fe-TAML/H_2O_2

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Vanilla is a well-known and in-demand commodity in industries all around the world. Vanilla originally comes from the vanilla orchid '*Vanilla planifolia',* which is native to Mexico. The fine chemical vanillin (4-hydroxy-3- methoxybenzaldehyde) is the primary component of natural vanilla. Vanilla comes from the pod or bean of the tropical *Vanilla planifolia*. Vanillin is mostly utilised in the cosmetics and perfume industries, as well as in the flavouring of ice creams, soft drinks, and appetizers. The demand for cured vanilla pods, which reached over 16,000 metric tonnes in 2015, exceeds the supply by a factor of ten. The emphasis has shifted to pure vanillin due to high prices and the failure of non-synthetic vanilla to satisfy the global demand for vanilla flavour [1].

Currently, all the vanilla beans in the world are insufficient to cope with the demand. Thus, synthetic vanillin is produced using different materials and methods. These include eugenols, petroleum and other chemicals which can produce vanillin with similar properties as vanillin from natural vanilla. Synthetic production of vanillin leads to environmental problems due to the release of hazardous by-products [1]. Thus, studies have been done to obtain pure vanillin from plant waste, the leaves of *Vanilla planifolia*, so that vanilla beans need not be used. With this, the demand for vanilla and the availability of vanilla sources may be balanced.

It is widely accepted that the chemical industry has an increasing need for more environmentally friendly methods to define the development of chemical processes and products that reduce or eliminate the usage or creation of hazardous compounds that are harmful to human health [2]. Green technology is an alternative to conventional extraction technologies which need a lot of solvent and have a longer processing time, causing high energy consumption. Green chemistry is the utilization of a set of principles that reduces or eliminates the generation of hazardous substances in the design, manufacture and application of chemical products. Several green technology methods can be considered as sustainable techniques to extract vanillin from the leaves of *Vanilla planifolia*, such as Microwave-Assisted Extraction (MAE), Microwave Pretreatment (MW), Ultrasound Technology and Subcritical Water Extraction (SCW). Besides these, green chemical oxidation using a Fe-TAML/H2O2 catalyst to treat the leaves of *Vanilla planifolia* is a recent promising technique to obtain high purity vanillin. There are very few literature reviews on this oxidation method, thus this review provides relevant information.

Novel Methods for Vanillin Extraction

Microwave-Assisted Extraction (MAE)

Novel green extraction strategies are evolving, with the goal of recovering important compounds in a sustainable and selective manner while overcoming the constraints of old methods, taking into consideration environmental, economic, and technical risks. In order to isolate bioactive substances derived from natural matrices, extraction is a crucial step. Microwave-Assisted Extraction is an effective approach to green chemistry because it is a totally environmentally friendly technique. Microwave energy has been used to enhance the extraction of natural compounds due to its ability to penetrate samples directly and interact with the polar components. As it interacts with the reaction molecules in the sample, heat is generated, which leads to a rapid rise in temperature. Microwaves have been used to improve many extractions of bioactive compounds [4].

Principles and Mechanisms of MAE

Microwaves are non-ionizing electromagnetic waves that range in frequency from 300 MHz to 300 GHz [5]. Microwave radiation has a suitable frequency for oscillating polar particles and allowing for sufficient inter-particle interaction. Thus, microwaves are suitable for heating polar solutions. Ionic conduction and dipole rotation are the two principles that regulate microwave heating [6]. These two mechanisms occur simultaneously and cause a transfer of energy. When electromagnetic waves are applied, the ions migrate through the solution and cause homogeneous heat in the medium due to the solvent's resistance towards ionic migration. This mechanism is known as ionic conduction. Microwaves generate an alternating electric field, to which dipolar molecules are sensitive. In the presence of this electric field, the dipole molecules reorient themselves in the direction of the electric field. The molecules rotate quickly, vigorously changing direction. Collisions between molecules generate heat. Energy transformation occurs from electrical energy to kinetic energy, and heat is transferred from the inside of the equipment to the outside. The heat transfer from the microwave energy causes the moisture in the plant matrix to evaporate and increase the pressure inside the matrix. This causes cell walls to rupture, releasing high-value compounds. There are two types of microwave methods for extracting bioactive chemicals, depending on how microwave radiation is supplied to the sample. One is the multimode system, in which microwave radiation is distributed randomly in a cavity to uniformly irradiate the sample. The other method is the single mode, in which microwave radiation is focused on a small area where the sample is irradiated more strongly than in multimode systems [6].

MAE can be performed using both open vessels and closed vessels. Closed MAE equipment is usually used for extraction under extreme conditions like high temperature, while open vessels are used for low-temperature extraction. Microwave devices consist of four major components: (1) a magnetron or microwave generator, (2) a waveguide to allow the propagation of microwaves, (3) a vessel containing the sample, and (4) a circulator which only permits microwaves to pass through [7]. In the vanillin extraction process, the leaves of *Vanilla planifolia* need to be ground and loaded into the vessel. Then solvent is added, and the vessel is closed before microwave radiation is applied to the sample. In order to heat the solvent to the desired temperature, pre-heating is performed. The sample is then further irradiated. After the extraction process, the sample is left to cool down. Microwave-assisted extraction differs from Soxhlet and heat-flux extractions, where the intracellular contents are washed out of the plant matrix through a series of permeation and solubilization processes.

There are several parameters that affect a microwave extraction such as pH, temperature, extraction time, extraction cycles. The nature of the sample matrix, solvent and particle size are also factors that influence microwave extractions. For MAE, there must be enough solvent volume to fully immerse the sample during the irradiation process. Low extraction yields may be obtained using large solvent volumes due to uneven distribution and microwave exposure, which requires more time and energy to condense the extract [8]. Small particle size increases extraction efficiency since the solvent contact surface area is larger and microwave penetration is higher. Before conducting MAE for vanillin extraction, the leaves of *Vanilla planifolia* must be completely ground and homogenised to increase the contact surface area between the solvent and the matrix. In a closed vessel MAE, temperature becomes a critical aspect since it contributes to better phytoconstituent recoveries [9]. The extraction efficiency increases as the temperature rises to an optimum value. The coefficient of molecular motion and diffusion increases significantly with temperature. Solvents with a higher solubility have a higher temperature. The extraction efficiency appears to decrease as the temperature increases above the optimum value.

On prolonged exposure to microwave radiation, the chemical structure of active compounds may be lost.

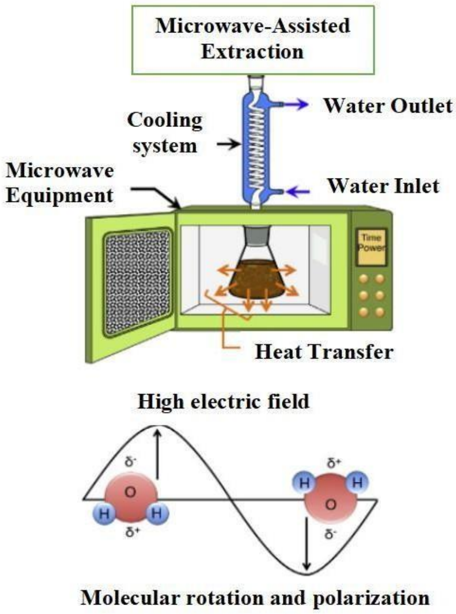

Figure 1. MAE equipment demonstrating the molecular rotation mechanism [10].

Advantages of MAE

MAE eliminates the use of chemicals and produces no waste, making it an environmentally beneficial method [11]. When compared to conventional technologies, MAE allows for a greater release of chemicals from the matrix of interest while minimizing extraction time and solvent usage [12]. By reducing extraction time, oxidation and thermal degradation can be avoided. Microwave-enhanced chemical reaction rates have been found to be 1,000 times faster than those of traditional heating methods based on experimental results [2]. It was reported that MAE recovered 92.1% of artemisinin from *Artemisia annua* L. in 12 minutes, while Soxhlet extraction could only achieve 60% recovery after a few hours [13]. Microwave heating improves the extraction process and saves a lot of energy compared to traditional heating. This is because microwaves only heat the sample and not the device, resulting in lower energy utilization. Microwaves produce uniform and selective heating. In traditional heating, the oil bath's walls are heated first, followed by the solvent. As a result, there is often a temperature differential between the walls and the solvent in an oil bath. Only the solvent and solute particles are excited in microwave heating, resulting in an even heat distribution.

Other advantages of MAE over conventional heating are: low operating cost, uniform heating throughout the matrix, elimination of unwanted side reactions, improvement in reproducibility and no heat loss. Furthermore, MAE may be applied in the industrial sector which would increase revenue because the extraction yield is much higher than with traditional approaches [14].

In terms of solvents used for MAE, the range of solvent polarity is wider. Some articles report that a mixture of water and ethanol is one of the most suitable solvents for the extraction of plant components as it is eco-friendly. The choice of solvent is determined by the solubility of the extracts of interest. The dielectric constant of the extraction solvent mixture significantly affects the efficacy of the MAE. The solvent should have a high dielectric constant and be able to absorb a lot of microwave radiation. Polar solvents with high dielectric constants include ethanol, methanol, and water. To enhance solvation power and improve the efficiency of MAE, both non-polar and polar solvents are incorporated for extraction. In addition, microwave irradiation accelerates cell wall breakdown and powdered sample pre-treatment makes the sample more sensitive to microwave heating. These may be incorporated into the MAE method, which can improve extraction rate and efficacy [15-16].

Recent research studies and reviews from scientists have illustrated the advantages and efficiency of using MAE. In comparison with other techniques for the extraction of vanillin, MAE had the highest extraction power and the shortest extraction time [17]. In Soxhlet and batch extractions, a large amount of solvent was required [9]. However, with MAE, a small amount of solvent was sufficient to achieve the highest *Marmelosin* yield. MAE (using 80% methanol) could reduce the extraction time of ginseng saponins to a few seconds, compared to 12 hours using traditional extraction methods [18]. With the aid of microwave energy, cocaine was extracted from leaves in 30 seconds, yielding results that were quantitatively similar to those obtained after several hours of conventional solid-liquid extraction [19]. Therefore, based on the literature, MAE may be a feasible method to obtain vanillin from *Vanilla planifolia* leaves.

Instead of a full-time MAE technique, several studies have also indicated that the implementation of microwave pre-treatment improved extraction efficiency and extract purity. Microwave irradiation prior to extraction resulted in a significant reduction in extraction time, increase in extraction yield, and a decrease in the amount of extraction solvent used. By using an intense but short microwave pre-treatment, the material was able to absorb an amount of energy equivalent to milder MAE radiation. A previous study found that microwave pre-treatment extraction of grape pomace resulted in an increase in the efficiency of the process as well as the bioactivity of the product [3]. However, no studies have been done on the extraction of *Vanilla planifolia* leaves to date.

Limitations of MAE

Although MAE is an advanced technology, there is still a gap in the scalability as the yield obtained after extraction is limited to a few grams. There are also limitations on the safety hazards of microwave equipment. Uncontrolled reactions involving volatile reactants at superheated settings may result in explosive circumstances if used inappropriately [20]. In addition, solids or unwanted material must be removed from the solvent, which necessarily involves a separate separation procedure.

Ultrasound-Assisted Extraction (UAE)

Ultrasound was shown to be a powerful instrument in achieving the goal of sustainable green chemistry and extraction. This technology can be used to produce a variety of phytochemicals, the most notable of which are phenolic compounds. The use of ultrasound for extraction has grown in recent decades as a result of the numerous drawbacks associated with traditional methods. In addition, this technique is generally simple to utilise, adaptable, scalable, and requires a minimum upfront outlay compared to other innovative extraction procedures. Sir Isaac Newton initially proposed his theory of sound waves in 1687, and the history of scientific advancements and the discovery of ultra-sound is anchored in the study of sound [21]. Recent studies have been focused on developing ultrasound technology for plant extractions [22]. In herbal phyto-chemistry, ultrasound treatment has been used for the detection of herbal bioactive compounds. Jadhav et al. (2009) discussed the extraction of vanillin from vanilla pods and compares four extraction techniques [23]. They showed that ultrasound-assisted extraction always gave high vanillin yields and required less time for the process to complete.

Principles and Mechanisms of UAE

UAE is based on the theory of acoustic cavitation, which causes disruption to plant matrix cell walls, allowing bioactive substances to be released [24]. Acoustic cavitation is the process of microbubble formation, expansion, and implosive collapse in ultrasound-irradiated liquids. Ultrasound waves propagate within the frequency range of 20 kHz to 100 MHz. It propagates by generating a series of compression and expansion waves in a liquid medium. When a high acoustic force is applied, cavitation bubbles are formed. These cavitation bubbles release a lot of energy and generate a lot of pressure and extremely high temperatures in specific areas [25]. The cavitation bubbles induced by ultrasound depend on characteristics such as frequency, viscosity, surface tension and ambient conditions, temperature and pressure. With an increase in ultrasonic frequency, the size and radius of the cavitating bubbles decrease, whereas an increase in ultrasonic strength results in an increase in the number of cavitating bubbles. Shear rupture, cell membrane weakening, and cell disruption are all caused by the temperature and pressure changes generated by these implosions, resulting in enhanced solvent penetration into cells and improved mass transfer of target material into the solvent. Finally, as a result of the oscillation phenomenon, the cavitation bubbles collapse into the fluid due to shear stress. The principle and cavitation phenomenon of the UAE is illustrated in Figure 2.

An ultrasonic device can give good yields in a short time using green solvents. While the technology has a huge amount of potential, it will need to be carefully built and scaled up for commercial use. The most fundamental part in the generation of ultrasound is a transducer which transforms electrical pulses into the necessary amount of acoustic energy. There are two types of transducers that are used to generate ultrasound energy, magnetostrictive and piezoelectric. The role of the transducer is crucial in deciding extraction yields and is essential for extraction efficiency, process intensification, and energy waste reduction [24]. Transducers may be located on either side of the extraction vessel, allowing ultrasonic waves to pass through the vessel's outer wall. Ultrasonic extraction equipment, whether bath or probe-type, is commercially available and operates at different frequencies. Magnetostrictive transducers generate ultrasonic waves by acting as electroacoustic transducers. These transducers operate on the magnetostriction principle, which is defined as the subsequent change in length per unit length [26]. A transducer is a device that converts acoustic and electrical energy. When a quartz crystal or other piezoelectric material is subjected to a force, it generates electrical charges on its surface, known as piezoelectricity, which is considered to be the cause of the cleaning process [27]. When transducers are in direct contact with the material in the presence of a suitable solvent, extraction efficacy improves while acoustic energy losses are reduced.

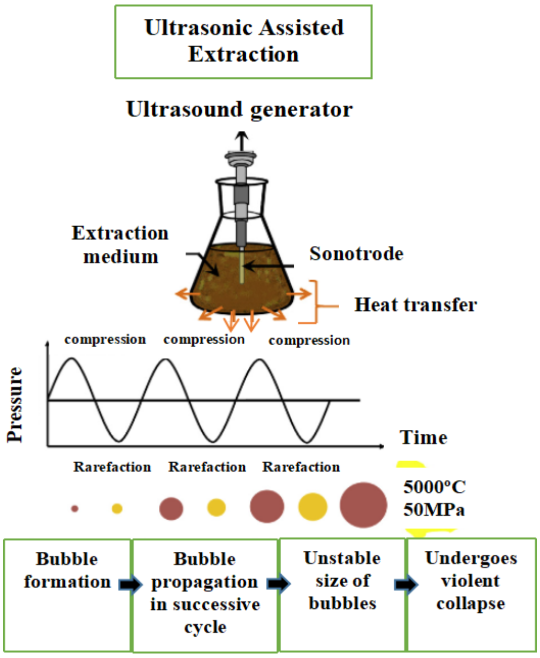

Figure 2. UAE principle and cavitational phenomenon [10].

Figure 2. UAE principle and cavitational phenomenon [10].

Advantages of UAE

As mentioned above, UAE is an advanced green technology for the extraction of plant components. Thus, UAE possesses many benefits, one of the most prominent being the increase in yield of extracted chemicals. The localized stirring that happens as a result of cavitation during ultrasonic extraction aids this physical separation even more. The benefits of UAE have been highlighted in several recent papers. It has been found that ultrasonic energy is useful in the extraction of vanillin from cured beans, as it increases diffusion rates by removing mass transfer resistance, resulting in a significant increase in extraction efficiency. The coupling of this stirring effect and repeated solvent washing of the vanillin was substantially superior to the simple washing strategy used in Soxhlet extraction [23]. Applying the ultrasonic technique at room temperature for the extraction of chlorogenic acid (CA) from *Cynara scolymus L.* (artichoke) leaves for 15 to 20 minutes using 80% methanol resulted in a significant increase in yield of up to 50% compared to room temperature maceration. The yield was comparable to that obtained by boiling for the same length of time [28]. UAE also requires less time and consumes less energy. The rate of extraction was faster with ultrasound than by Soxhlet extraction in all the cases analysed. It was claimed that conventional extraction took 8 hours to release around 180 ppm vanillin at 95 °C and a solvent to solute proportion of 66.67 ml/g, but ultrasonic-aided extraction took just 1 hour to release around 140 ppm vanillin at similar solvent to solute proportions and at room temperature [23]. Other reports also proved that ultrasound improved product quality, reduced processing time, and reduced fresh leaf processing costs [29]. In addition, ultrasound improved the yields and extraction efficiency of total polyphenols and flavonoids from *Serpylliherba*. When designing a safe, green UAE system, there are many factors to consider. To prevent unfavourable degradation of the extracted compound, the best frequency conditions must be chosen. To control the cohesive forces of the solvent and the sample, ultrasonic intensity should be enhanced as frequency is increased to attain the desired cavitation. For example, 10 times more power is needed to create cavitation in water at 400 kHz than at 10 kHz [30]. Due to sound energy, temperature change is unavoidable during the extraction process, and in most situations, increasing the temperature speeds up reaction rates. Temperature can be controlled externally during extraction by distributing cold water. Most reported extraction temperatures range from 10 °C to 80 °C, based on ultrasonic intensities and solvent [24]. The productivity of ultrasound extraction was compared to that of other traditional methods. Approximately 65% recovery of anthraquinones from the roots of *Morinda citrifolia* was obtained by UAE at a temperature of 60 °C using pure ethanol for 60 min [31].

Limitations of UAE

Scaling up from the laboratory to the industrial scale is one of the major issues of UAE. Not only is it not cost-effective to simply increase the size of the vessel and ultrasonic instrument, but it also creates major construction issues because UAE is a non-linear method. High intensity ultrasound produces heat and raises the temperature of the treatment medium, which may have negative physical and chemical effects on certain plant phytochemicals. Before applying ultrasound to various plant tissues, the strength and energy of the ultrasound should be optimized.

Subcritical Water Extraction (SWE)

Subcritical water extraction is a green technology that takes advantage of the distinctive features of subcritical water, such as hot water exceeding boiling point under high temperature-pressure conditions just below its critical point (374 °C, 220 bar). The temperature and pressure ranges for SWE are (100–250 °C) and (1–8 MPa) correspondingly [32]. SWE has been shown in several studies to have short extraction times, lower solvent consumption, high selectivity, and be able to extract fractions with diverse compositions and high biological activity. Some of the most recent studies include the subcritical water extraction of plant bioactive compounds from plant sources like *Eucalyptus* leaves [33], dry and fermented orange pomace [34] and *Eugenia involucrate* leaves [35].

Principles and Mechanisms of SWE

In SWE, water is pressurised to a temperature and pressure below its critical level. The operational pressure is kept constant above the vapour pressure to keep the water in a liquid form in subcritical circumstances [36]. Water boils to produce water vapour when functioning below the vapour pressure, and this vaporisation process raises the pressure above the vapour pressure level, leaving the water in a liquid state. The mechanisms involved in the SWE process are diffusion, partitioning equilibrium, and convection to transfer solutes from the various active sites in the sample matrix to the extraction medium [37]. The external mass transfer through a liquid film is the most important step in this mechanism where the elution of the solutes from the matrix occurs, whereas the rate-limiting mechanism for SWE has been recognised as the solute partitioning equilibrium between the solvent and the solid matrix [38]. Temperature has the most profound effect on the thermodynamic properties of water. The strength and structure of hydrogen bonds are commonly used to express these properties. These bonds are linked to one another; as a result, the strength of one bond has an impact on the surrounding bonds. As water temperature rises, the stability of hydrogen bonds decreases, resulting in a drop in the polarity of water and its dielectric constant. These values become similar to those of organic solvents like methanol and ethanol at ambient temperature under subcritical conditions due to an increase in molecular kinetic energy. For example, the dielectric constant of water decreases from 79 to 35 as the temperature rises from 25 to 200º, whereas the dielectric constants of ethanol and methanol are 24 and 35 at ambient temperatures, respectively [39]. As a result, at subcritical temperatures, water behaves like a mixture of water and organic solvents, increasing the solubility of less polar substances. As the temperature rises, the viscosity and surface tension of the water decrease, resulting in a faster rate of mass transport and diffusivity [40-41].

SWE can be used in batch or continuous systems, but the continuous system is the most current. The extraction bed is fixed in this system, and the flow direction is usually up to down to allow for easy analyte cleaning. Even though SWE equipment is not commercially available, the apparatus is simple to build in the lab. A schematic diagram of this apparatus is illustrated in Figure 3.

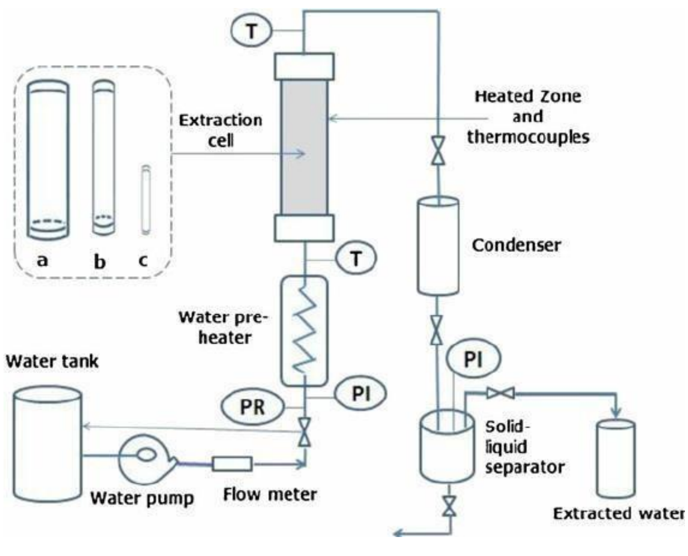

Figure 3. Schematic diagram of SWE system [38]

A dynamic SWE unit consists of three tanks, two pumps, an extraction vessel, an oven for heating the extraction vessel, a heat exchanger for cooling the extract, a pressure restrictor, and a sample collection system. The extractor can perform SWE, which involves a series of steps that take place in a sample-filled extraction cell. Fast fluid entry, solute desorption from matrix active sites, solute diffusion through organic materials, solute diffusion through static fluid in porous materials, solute diffusion through a layer of static fluid of external particles, and solute elution by the flowing bulk of fluid are some of the steps that have been found [38].

Advantages of SWE

Environmental compatibility, shorter extraction times, better yields, higher quality and purity of the extract, lower solvent supply and disposal costs are all advantages of SWE over traditional methods [42]. In comparison to other extraction techniques, SWE allows higher diffusion into the plant matrix and has increased mass transfer properties. SWE can reduce extraction times by up to 50% of conventional method extraction times [43]. Generally, SWE had higher extraction yields than traditional methods like Soxhlet, hydrodistillation, and supercritical fluid extraction. Traditional extraction procedures are inefficient and time-consuming, as well as non-selective. Toxic solvents are also required for these traditional methods. The major benefit of using subcritical water is that water is a safe solvent that can replace toxic organic solvents, particularly in the case of food and pharmaceuticals that require solvent removal after extraction, which is a time-consuming and costly process. Water is also a cheap and easily available solvent. The retrieved extracts are completely safe, as they contain no toxic residues. Moreover, low-polar and non-polar compounds can both be extracted using SWE. SWE has drawn a lot of attention, especially because of the significant change in water properties caused by temperature changes. Water is an extremely polar solvent at ambient temperatures, with a dielectric constant of around 80 indicating its polarity. In this condition, water is favourable for the extraction of highly polar compounds. However, when water is heated to between 100 ˚C and 374 °C and placed under enough pressure to keep it liquid, its polarity decreases significantly, making it suitable for the extraction of both polar and non-polar compounds. This is due to the significant decrease in the dielectric constant as the temperature rises. The surface tension, viscosity, density, and polarity of water are all significantly reduced at elevated temperatures in the subcritical state. The surface tension of water decreases at higher temperatures, allowing for better wettability of the extracting material and faster solubilization of targeted compounds in the solvent. Water with a lower viscosity penetrates more deeply into the extracting material, improving the rate of diffusion. As a result of the increased diffusion rate, extraction can be completed more quickly [44].

Many studies have revealed that SWE extraction of phenolic compounds is more efficient than traditional extraction methods. The efficiency of SWE was compared to traditional extraction technologies in a study and it was found that SWE yielded four times higher concentrations of quercetin compared to other extraction technologies using methanol and ethanol as solvents [45]. An investigation on anthocyanin extraction from fruit berry substrates found that SWE produced equivalent or superior results to conventional ethanol extraction [46]. According to Soto Ayala and Luque de Castro, the cost of extraction is clearly advantageous for SWE and this feature is critical for future industrial implementation [47]. SWE also has a great advantage in respect to extraction time. SWE shows shorter extraction times compared to conventional methods**.** SWE was used to extract phenolic compounds from *Terminutesalia chebula* Retz fruits [48]. The extraction methods of SWE and Soxhlet were compared in this study. The results showed that SWE hydrolysis only took 37.5 minutes to recover a significant amount of phenolic compounds, whereas Soxhlet extraction required more than 2 hours of reaction time to achieve the maximum yield of phenolic compounds [49].

Most compounds that are soluble in methanol or aqueous ethanol, such as flavonoids, polyphenolic compounds, and triterpenes, have been successfully extracted using SWE. The use of SWE extraction produced higher yields of phenolics (81.83 mg/100 g) than the yields obtained with methanol extraction (46.36 mg/ 100 g) or with ethanol extraction (29.52 mg/ 100 g) [50]. SWE was able to recover 96.3% of the flavonoids from dried satsuma mandarin peel in the pilot plant with an extraction temperature of 130 °C, extraction time of 15 minutes, and solute/solvent ratio of 1/34 [51]. SWE produced high yields of pentacyclic triterpenoids from dry loquat (*Eriobotrya japonica*) leaves (25.02 ± 0.71 mg/g) obtained at 200 °C, 41.67 mL/min with an extraction time of 30 min compared to 4 h with conventional solid-liquid extraction (14.39 ± 1.12 mg/g) [52]. Thus, based on the high demand for safe extracts from natural sources, SWE has a strong chance of becoming a viable alternative for obtaining vanillin from *Vanilla planifolia* leaves.

Limitations of SWE

Even though water is the most environmentally friendly solvent for extracting bioactive compounds, it has drawbacks in terms of operating costs. Water-based extracts, as well as concentration techniques to remove water from the extracts, have been found to be time-consuming and tedious. This is because water evaporation generates a significant amount of heat in comparison to the heat of vaporization of many organic solvents. Furthermore, the presence of water may weaken the stability of the extract [44]. To achieve a concentrated extract adequate for freeze-drying, concentrating water in a rotary evaporator at a lower pressure is a required step. Since liquid is removed without a phase change, freeze-drying is employed for heat-sensitive items. Thus, freeze-drying is one method to dry subcritical water extracts, though it is costly and time-consuming. The heat, light, and oxygen may also cause bioactive substances to breakdown. Since the active ingredients in crude plant extracts achieved by SWE were found to be complex and similar, the desired purity could not be achieved by solely using the SWE technique. This implies that the development of SWE may necessitate the incorporation of a clean-up step [52]. When it comes to the temperature sensitivity of the bioactive compounds to be extracted, SWE extraction conditions vary greatly. Working under optimal extraction conditions can solve this problem [53]. Despite the challenges, SWE appears to be a viable green extraction technique with a great future compared to other traditional extraction methods.

Comparison of MAE, UAE and SWE

Overall, most studies report that the MAE, UAE and SWE techniques result in good extraction efficiency, processing time, energy consumption, and reduce the use of harmful and expensive solvents. The major drawbacks of conventional extraction technologies which include longer extraction times, the need for expensive and high purity solvents, evaporation of a large volume of solvent, poor extraction selectivity, and thermal decomposition of thermolabile compounds, have been solved by these green technologies. The extraction yield obtained totally depends on the operating conditions and parameters such as temperature, time, solute/solvent ratio, power, and amount of solvent.

In terms of phenolic content in several plants, MAE showed better results than UAE. MAE had a number of benefits, including a shorter time, a greater extraction rate, reduced energy use, and improved product yield. Water has proven to be an effective solvent in SWE under subcritical conditions. Water diffusion increased with temperature, implying that hot water aids in the easy release of components from the plant matrix during the solid-to-liquid mass transfer mechanism in SWE. Since water is the greenest solvent, SWE is an environmentally safe and effective alternative method for extracting bioactive compounds from solid plant samples that result in higher extraction yields. However, the drawbacks of this technique are higher compared to MAE and UAE. Such limitations include the fact that the presence of water may weaken the stability of the extract and that additional steps are required to dry the extract. MAE shows fewer drawbacks than the other methods and thus, it is the best method overall. However, as discussed in this paper, there are a few limitations and challenges in implementing these green technologies. Such limitations include scalability to industrial applications, construction issues to increase the size of the equipment to industry scale, cost, clean-up steps that require procedures to remove water from the extract to obtain concentrated extracts in subcritical water extraction and phytochemical degradation caused by elevated temperatures. Thus, microwave pre-treatment and green chemical oxidation are two green technologies introduced to overcome the limitations of other green technologies. In recent studies, a new catalyst also known as a 'green catalyst' (Fe-TAML/H_2O_2) has been reported to improve the quality of the yield obtained. This green catalyst is environmentally benign, cheap, minimizes the number of steps in the process and does not require a clean-up procedure.

Table 1. Comparison of MAE, UAE and SWE

	MAE	UAE	SWE
Phenolic content	Higher	Lower	Lower
Extraction time	Shorter	Longer	Longer
Extraction rate	Higher	Lower	Lower
Energy use	Lower	Higher	Higher
Green solvent	No	No	Yes (water)
Drawbacks	Few	Moderate	Most

Microwave Pre-treatment

Microwaves are electromagnetic waves that exist in the electromagnetic spectrum between infrared and radio waves. To extract vanillin from the leaves of *Vanilla planifolia*, a pre-treatment process is necessary to prepare a quality sample prior to extraction. The pre-treatment process involves irradiating extraction media with a short but high-energy pulse, resulting in a rapid temperature rise. To avoid degradation reactions, the sample is rapidly cooled after the pre-treatment. The high yield obtained after extraction is one of the most satisfying advantages of the microwave drying process. Extraction with new and moist leaves is only possible in a few situations. As a result, microwave pre-treatment is needed to fully dry the leaves in a short time. This has the potential to improve extraction performance.

Several research studies have shown that microwave pre-treatment improved extraction efficiency and extract purity. Microwave pre-treatment has been used to dry grape pomace as well as to obtain polyphenol extracts. The results show that microwave pre-treatment increased not only the efficiency of the process but also the bioactivity of the product. These polyphenol and anthocyanin-rich extracts were found to have a higher level of cellular antioxidant activity against peroxyl radical harm. The addition of microwave pre-treatment doubles the bioactivity of the finished product [3]. In this work, instead of a full-time MAE technique, a brief microwave pre-treatment is proposed as a preface to the conventional extraction. A short residence time pre-treatment will enable the material to be irradiated evenly in a microwave appliance of acceptable size. Furthermore, the material will have the ability to absorb a certain amount of energy equal to milder MAE radiation conditions by using an extreme but brief microwave pre-treatment. The extraction must be improved in terms of yield and quality. Therefore, it has been shown that conducting microwave pre-treatment before the extraction process improves the process yield and product quality in order to obtain the desired pure compounds. From this, we can assume that conducting microwave pre-treatment on the leaves of *Vanilla planifolia* before proceeding to the extraction process could achieve similar results as studies done on other plant sources. The improvement in the stability and functionality of the product obtained would be suitable for commercial use.

Green Chemical Oxidation

Green Chemicals

Green chemicals are chemicals that are both environmentally friendly and perform well over their entire life cycle. The Twelve Principles of Green Chemistry are a set of guidelines for green chemicals. Green chemistry is the natural development of pollution management measures of sustainability in the corporate and regulatory areas. Green chemistry has become important in all industries to stop unintentional harm to nature and the environment in the pursuit of better commercial goods, agriculture, and medicine.

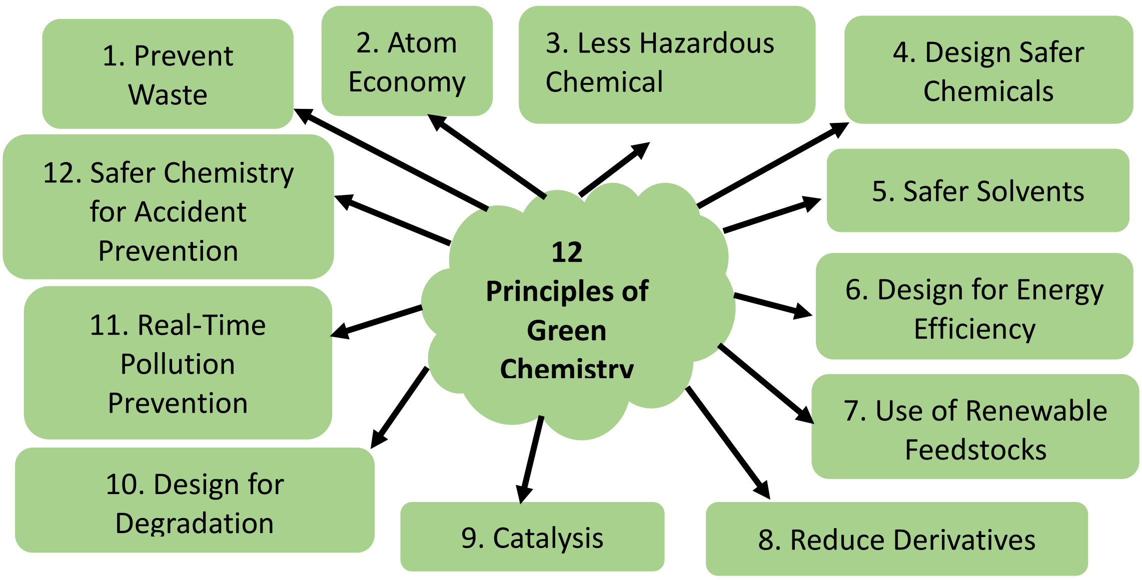

Figure 4. 12 Principles of Green Chemistry

The Design of Fe-TAML Peroxide Activating Catalyst

Fe-TAML (iron (III) tetraamido macrocyclic ligand) was patented by a team at Carnegie Mellon University's Institute for Green Oxidation Chemistry led by Terrence Collins. An iron atom lies in the centre of the Fe- TAML molecule, which is surrounded by four nitrogen atoms and a ring of carbon atoms. Water molecules attach loosely to the iron atom's vertical pole as a ligand. Hydrogen peroxide (H2O2) is a chemical compound made up of hydrogen and water. In its pure state, this is a pale blue, transparent substance that is slightly more viscous than water. Hydrogen peroxide is the most basic peroxide. It is a bleaching agent, an oxidizer, and an antiseptic. Hydrogen peroxide can be broken down to produce water and oxygen. The heat and energy that are spontaneously created demonstrate that hydrogen peroxide is thermos-dynamically unstable. Hydrogen peroxide is also regarded as a "natural" oxidant, but its relatively high cost has restricted its use in commodity chemical manufacturing. Hydrogen peroxide is considered a green oxidant because it is relatively non-toxic and breaks down easily into harmless by-products.

Researchers discovered that Fe-TAML activators and hydrogen peroxide appear to fully break down lignin and cellulose in plant leaves. TAML activator/peroxide devices are directly or potentially applicable in a variety of areas, including the pulp and paper, water treatment, textile, petroleum refining, and chemical industries as well as biological terrorism. Thus, for obtaining vanillin from the leaves of *Vanilla planifolia*, it is beneficial to treat the leaves with Fe-TAML/H2O2 before proceeding with extraction procedures. This will increase the purity of the yield obtained without any residual contamination.

For production, tetradentate ligands were selected to leave one to two coordination sites available for coordination and activation of hydrogen peroxide on a transition metal ion [54]. To avoid Fenton chemistry, which happens when metal ions mix with peroxides to generate a highly toxic hydroxyl radical, the peroxide activating the catalyst should be designed first. Understanding the origins of lifetime regulation in functional enzyme oxidation is just as important as understanding the origins of sustainable chemical technologies.

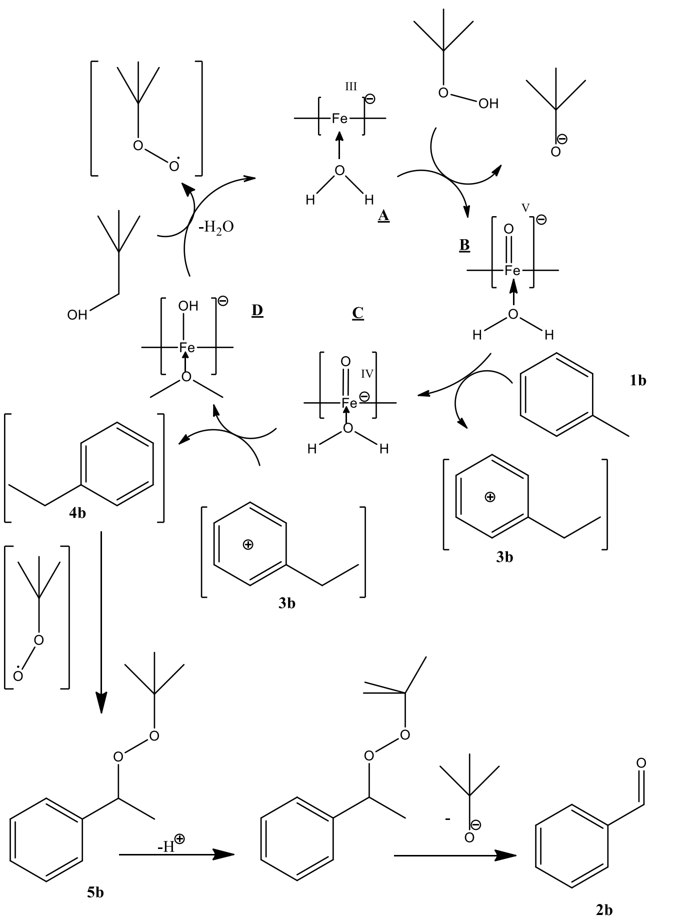

Figure 5. Mechanism of Fe-TAML catalyst with H_2O

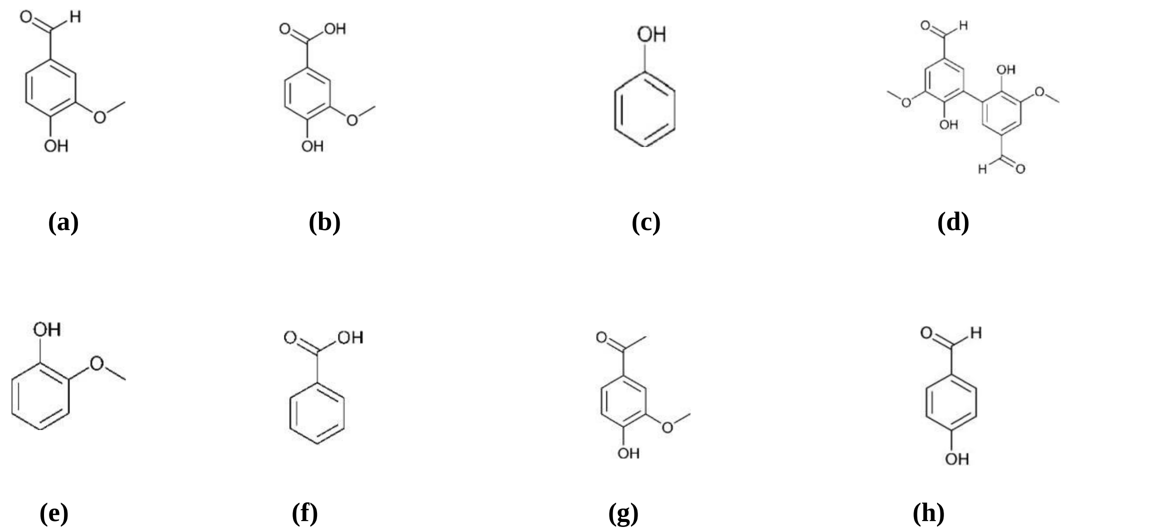

Figure 6. Possible compounds extracted from *Vanilla planifolia* leaves treated with Fe-TAML/H2O2 catalyst: (a) Vanillin (b) Vanillic acid (c) Phenol (d) Dehydrovanillin (e) Guaicacol (f) Benzoic acid (g) Acetovanillone (h) *p*-hydroxybenzaldehyde

In Figure 5, process A demonstrates a system involving Fe^{III} and water. In addition to oxidising peroxidase-like substrates, the reactive oxo-complex active catalyst (AC) can also degrade peroxide. Since the active catalyst is unable to attack or lose the electron donor's difficult-to-oxidize substrates, competition from the catalase process (B) could become very intense. The catalyst can be eliminated by medium-induced degradation (A), such as hydrolysis and intramolecular and intermolecular suicide inactivation. It causes rapid hydrolysis of the remaining three Fe-N bonds by cleaving a single Fe-N bond. The Bronsted acid components of a buffer solution will demetallize the complex. Since Fe^{III}-TAML converts H2O2 to H2O and is degraded by B and D, no reactive treatment reagent is released into the environment.

Catalytic Oxidation System for Vanillin Production

The typical experimental procedures to treat the leaves of *Vanilla planifolia* are proposed with certain treatment conditions. A typical reaction take place at 25 ºC, with a sample of ground leaves placed in a 100 mL beaker to which a carbonate buffer solution (20.0 mL of a 0.010 M solution, pH 9.5) was added. The mixture was stirred using a magnetic stirrer bar. The aliquots of standard Fe-TAML solution and standard H2O2 solution were then added to the mixture in no particular order. The mixture was left for one hour. To decompose the hydrogen peroxide into water and oxygen and to stop the reaction, catalase was added. To study the effect of the catalyst on the production of vanillin, different concentrations of solution may be used. The pH may also be altered to alter the reactivity of the Fe-TAML catalyst, as it is pH dependent. As a result of the proposed method, a notable amount of vanillin can be obtained. However, other possible compounds could also be formed besides vanillin such as dimers, phenolics and carboxylic acids.

Advantages and Limitation of Fe-TAMLs

TAMLs work by imitating the enzymes that have adapted in our bodies to combat toxic compounds over time. TAMLs have been shown in lab and real-world trials to be able to remove toxic pesticides, dyes, and other toxins, significantly reduce the odour and colour of wastewater emitted by paper mills and destroy bacterial spores indistinguishable to those found in the fatal anthrax strain. Carbon, hydrogen, oxygen, nitrogen, and iron are all employed in TAMLs because of their low toxicity. These elements are engineered to search out and lock onto particular contaminants. While further toxicity testing is required, the results so far show that TAMLs break down contaminants into nontoxic constituents, leaving no detectable pollution [55]. Moreover, TAMLs are also cost-effective as they can render huge clean-up processes unnecessary.

There are several studies on the application of Fe-TAML catalysts in the industrial sector. Research has been carried out on the oxidation of sulphur components in diesel fuel using Fe-TAML catalysts and hydrogen peroxide. It was reported that high internal reactivity of Fe-TAMLs against H2O2 and their substrate selectivity make them promising candidates for oxidative desulfurization of refined fuels [56]. A study was conducted on the utilization of a TAML/H2O2 catalyst to degrade a wide variety of aromatic organic contaminants (ACs) in wastewater matrices [57]. Wastewater treatment plants release treated water into the natural water system, which can impact aquatic ecosystems and human health [58]. After treatment with TAML/H2O2, the toxicity of polluted water was found to be considerably reduced, and residual amounts of TAML had no harmful effects on fish or microorganisms [59]. Therefore, this advanced oxidation method is able to remove traces of ACs in wastewater and contribute to a safer environment. Moreover, TAML/H2O2 catalysts can be used at a minimum concentration and achieve high efficiency in the oxidation process.

In the pulp and paper industry, the peroxide activator Fe-TAML either prevents the development of pollutants by eliminating the processes that produce them, or by swiftly extracting toxins from product effluents, the environmental impact of existing technologies can be minimized. Fe-TAML/H2O2 is used to eliminate the unappealing colour from chlorine-based bleaching methods used in paper mills, and also to remove some harmful chlorinated by-products [60].

One limitation of Fe-TAML catalysts is that they are highly dependent on pH. The rate constant studied reached a maximum value at ~ pH 10 and was lower at pH 6 and 7 [61]. This shows that the catalyst is active at only certain optimum pH values.

CONCLUSION

Plant-based extraction may be a major success of green chemistry in the twenty-first century, as well as a solution from the ancient past for the future of mankind in environmental and commercial chemistry. Green extraction of natural resources may be a new paradigm to address the demands of the twenty-first century, protecting both the environment and consumers while still increasing industry competitiveness to be more environmentally friendly, economically viable, and innovative. The ever-increasing demand for plant bioactive compounds necessitates a never-ending quest for efficient extraction methods. Based on the available literature on the advancement of green extraction technologies, microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), subcritical water extraction (SWE), microwave pre-treatment and green chemical oxidation using Fe-TAML/H_2O_2 catalysts have shown potential in obtaining desired bioactive and phenolic compounds from plant sources. In conjunction with green chemistry principles, replacing conventional techniques with non-conventional ones for the extraction of valuable compounds such as vanillin from leaves of *Vanilla planifolia* has significant advantages, including reduced energy consumption, non-toxic organic solvents and increased extraction yields. Most importantly it can minimize the number of steps as well as the clean-up process, which may attract the attention of the industrial sector. The working catalyst Fe-TAML/H_2O_2 is a crucial invention which brings numerous economic, environmental and commercial advantages. This new class of catalysts can remove some of the worst pollutants before they get into the environment. The leaves of *Vanilla planifolia* that are treated with Fe-TAML/H_2O_2 could produce high quality vanillin without any toxic effluents released to the environment. Moreover, these advanced green technologies for extraction are in accord with the Green Chemistry Principles, an important guideline for the process and development of new inventions in chemistry. The growing economic importance of bioactive compounds and bioactive compound-rich commodities could lead to the development of more sophisticated extraction techniques in future.

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