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Green Extraction Of Polyphenolics As Potential Bioactive Components From Pineapple Skin: A Review.

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ABSTRACT

Polyphenol is naturally occurring diversified molecular and different structure secondary metabolite found in plant. It is responsible for the color, flavor, astringency odor and oxidative stability in plant. In human also it's prevent from different degenerative diseases and diseases related to oxidative stress like cancer, cardiovascular, osteoporosis and neurodegenerative diseases. Therefore, researcher are showing interest to know the health benefits of each polyphenol present in plant, fruits and vegetables. However, waste generated from plant, fruits and vegetable also has potential to contain the polyphenol, one of such fruit is pineapple. Pineapple is very famous fruit cultivated worldwide and generate approx. 50% of waste as such or while processing in pineapple processing industries. Pineapple waste mainly consist of crown, skin (peel) and core. And each portion of waste has immense potential in term of natural occurring polyphenol. Through different studies it has confirm that pineapple peel is a good natural source of polyphenol which is ranging from 7.97 ± 0.63 to 10.62 ± 0.37 mgGAE/g dw. Polyphenol found in pineapple peel is extracted by using different extraction technique. Extraction technique are mainly conventional or non-conventional, non-conventional technique is most popular because it requires less time and solvent and having high extraction rate. However, non-conventional technique considered as green extraction technique. Some familiar green extraction techniques are Microwave assisted extraction, ultrasonic assisted extraction, enzyme assisted extraction, pulse electric filed assisted extraction and so on. Microwave assisted extraction and Ultrasonic assisted extraction both the technique again confirms the same that the pineapple peel is a good source of natural polyphenol. And extracted polyphenol is not only solve the environmental issues like waste management but also has lots of potential in different or new industries like food industries, pharmaceutical industries, therapeutic industries etc.

Keywords: Green extraction, polyphenolics, bioactive components, waste, pineapple skin

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INTRODUCTION

Polyphenol is naturally occurring secondary metabolite of plants having huge molecular diversity with different structure and function. It helps to protect from damaging radiation by absorbing UV light because of their aromatic properties. Thus, polyphenol has antioxidant properties which help to maintain the reduced redox status in plant. Polyphenol largely found in Vegetables, Cereals, fruits and beverages and also play an important role in food where they can be contributing or utilized as natural colorants, flavor, astringency, odor and oxidative stability. (KB Pandey & Syed Ibrahim Rizvi et al). However, the association of polyphenol in human health is very crucial because meta-analyses and epidemiological studies are strongly suggested that the consumption of plant polyphenol rich diets prevent or provide protection from some degenerative diseases and diseases associated with oxidative stress, such as cancer, cardiovascular, osteoporosis, diabetes and neurodegenerative diseases. (Dietmar R. Kammerer & others et al). Hence, researcher mainly focused or concentrating the health-beneficial effects of each phenolic compounds, extracted polyphenols form plant, fruits and vegetables in different test systems (in vitro / in vivo). The studies also comprise the bioavailability and bioactivity with the evaluation of the antioxidative properties under different condition that may consideration concerning the risk and safety aspect connected with consumption of polyphenol (Mennen LI Walker R & others et al).

Moreover, above 8000 polyphenolic compounds have been identified from the different plants origin and they are further classified into different groups based on the function and phenol rings found as structural elements. The main classification is consisting of Phenolic acids, flavonoids, stilbenes and lignans (Spencer JP & other et al) shown in fig 1. The main dietary phenolic compounds are Phenolic acids, flavonoids and tannins. Phenolic acids again divided into two subgroups, i.e hydroxybenzoic and hydroxycinnamic acid. Flavonoids class of polyphenol also consist of flavonols, flavones, flavanones, flavanols (catechins), isoflavones, flavanonols and anthocyanidins. (Hollman, P.C.H., Katan, M.B. et al).

It has already reported that the waste and by-product generated from fruits and fruits processing industries may be abundant source of the antioxidant polyphenols (Balasundram, Sundram, & Samman, 2006; Peschelet al., 2006). Therefore, the pineapple fruit waste and pineapple fruit processing industries waste has huge potential to develop new product for new industries by utilising or applying innovative methods of waste management. Pineapple are cultivated worldwide and India is one of the leading country to cultivate pineapple. Pineapple waste consist of a Crown, Core and peel. As a whole the generation of waste from pineapple is POFW (Pineapple on Farm Waste) and PPW (Pineapple Peel Waste) and it cause environmental pollution if not discarded properly. These waste contain good amount of bioactive compound or utilised as a raw material to extract polyphenolic compound, fiber, bromelain and organic acid. (R Salve & Subhajit Ray et al). However, utilisation of the polyphenol and other bioactive constituents for from pineapple waste have immense potential application in the field of Food Industry and Pharmaceutical Industry and other industry as well. It also addresses the environmental issues.

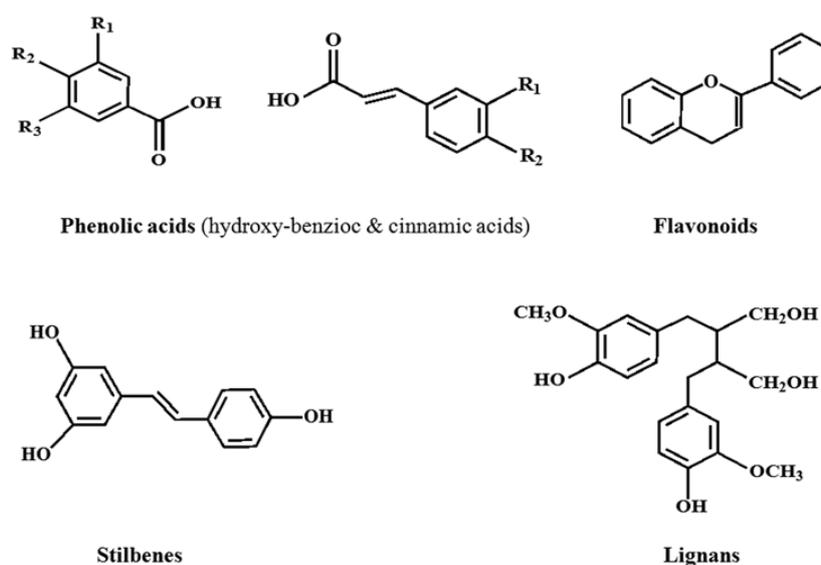


Figure 1: Polyphenols are broadly divided in four classes i.e Phenolic acids, flavonoids, stilbenes and lignans, based on the number of phenol rings and structural elements that bind these phenol ring to each other.

Polyphenol Content In Pineapple Waste

Pineapple waste included the Peel, Crown and Core (Fig – 2) all contains the valuable source of bioactive compounds (polyphenol), organic compounds, enzymatic activities, fibers so on and specially polyphenol shows immense beneficial properties like therapeutic use, anti-inflammatory, anti-microbial and most importantly antioxidant role of polyphenol (Namrata Yesh Sharma & Tripti Sharma et al). The total phenolic content (TPC) is differ from each other like Pineapple Crown is having highest TPC followed by Peel and Core as per the Table – 1 (Awanis Azizan & others et al).

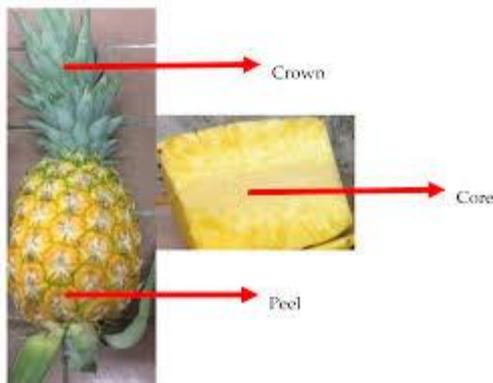


Figure 2: Pineapple waste (Crown, Peel and Core)

Pineapple peel is commonly used and more suitable for the phenolic extraction and also good source of gallic acid, catechin, epicatechin and ferulic acid (Lucia Panzella and Others et al). whereas crown waste is good source of polyphenol but mainly used as a substrate for the bromelain extraction and fiber extraction. Bromelain consist of peroxidase, numerous protease inhibitors and acid phosphate (Gardner et al., 2000).

Various studies also confirm that the Pineapple peel can be converted into potential source of antioxidant and gives high yield of phenolic extraction in 55% ethanol. (V Saraswaty and others et al)

Polyphenol / phenolic compound is extracted through different extraction techniques and using different solvents. However, to find out or to assay the TPC many researchers used different technique or methods with different standard or controls reagent or chemical available in market. Some extraction methods are conventional i.e soxhlet Extraction, Maceration and Hydrodistillation method and some non-conventional methods i.e Ultrasonic Assisted extraction, Microwave Assisted extraction, Enzyme-Assisted Extraction etc.

Table 1: Details of Total Phenolic Content (TPC) found in different portion of pineapple waste in mg GAE/g crude extract.

Part	Ethanol	Total Phenolic Content (TPC) (mg GAE/g crude extract)
	Ratio %	
Peel	0	10.62 ± 0.37
	50	10.73 ± 0.14
	100	7.97 ± 0.63
Crown	0	12.15 ± 0.62
	50	12.71 ± 1.15
	100	12.71 ± 1.15
Core	0	3.53 ± 0.12
	50	4.80 ± 0.23
	100	4.15 ± 0.20

SCAVENGING ACTIVITY ON DPPH RADICAL

One of the most important properties of antioxidant is free radical scavenging activities, which is very much important because of the harmful nature or role of free radicals present in biological system as well as in

foods. (Gulcin et al). DPPH (2,2-diphenyl-1-picrylhydrazyl) it is dark colour crystalline powder, act as a stable free radical and has the ability to accepts an electron or hydrogen and become a stable diamagnetic molecule (Soares et al). DPPH commonly used to investigate scavenging activity of radical and having various advantage of ease and most economical. In DPPH, free electron is present which get paired with antioxidant present in the sample and absorption decreases due to the DPPH's purple colour is converted to yellow. The degree of discoloration is directly proportional to the antioxidant presence or concentration. (Yingming et al).

DPPH radical scavenging activity calculate by the following equation:

$$\% \text{ DPPH radical scavenging activity} = \{(A_0 - A_1) / A_0\} \times 100$$

Where, A_0 = Absorbance of the control.

A_1 = Absorbance of the extractives / Standard

Percentage of inhibition is plot against the concentration and plot the graph IC50

POLYPHENOL / PHENOLIC EXTRACTION METHOD'S

Extraction, it is a systematic process of procedure follow to separating desirous solute with the help suitable solvent (Handa et al., 2008). There are Conventional and Non Convention methods of extraction. Conventional extraction methods are time consuming and require high amount of solvent and extraction is low. To overcome to this problems Non-Conventional extraction technique is replaced the conventional extraction technique, in non-conventional technique the extraction time is less and solvent requirement and sample requirement is also very less. Most importantly the extraction yield is very high. However, Non-conventional techniques are considering as a Novel or green extraction technique.

Some Non-technique are very useful to extract polyphenol compound from the pineapple peel and by which certainly confirm the pineapple peel waste is good source of polyphenol and can be utilized in new industries. Some Non-conventional techniques along with the test result is discussed.

Microwave Assisted Extraction (MAE)

Microwave assisted extraction (MAE) technique principally based on the dielectric heating, the process is dielectric material heated by the microwave electromagnetic radiation due to the dipole rotation of the polar compound / components present in the sample. (Ran X li et al). Microwave assisted extraction also considered as a green extraction technique because it reduces the extraction time and consumption of solvent is also less. The sample preparation for the Microwave Assisted extraction technique is generally followed the same step for the same preparation for the other non-conventional technique. It involves few step like (1) Cut the skin or peel form the whole pineapple fruit. (2) Wash the cut skin with distilled water and place the sample in deep freeze about -19 degree for the period of 24 hrs. (3) Again wash the sample with distilled water and place the sample in oven at 60 degrees for 48 hrs for drying. (4) finally make a dried powder or cut into small pieces approx. 0.5mm from the dried sample.

MAE consider as green technology it requires only 5gm of sample for the extraction. Thereafter, experiment set up and the steps may varies depend upon the Lab requirements and the different parameters. the details of different set up is mention in Table -2

Table 2: MAE test result at different Power, Temperature and Solvent Concentration.

Nor Halaliza Alias and Zulkifly Abbas et al				
Power	Temp °C	Solvent	Phenolic content (mgGAE/g dw)	DPPH activity (mg/mL) EC/50
250 W	30	Ethanol	118.02	98.04
	30	Water	206.46	13.65
	60	Ethanol-Water (50-50)	173.94	19.14
	90	Ethanol-Water (50-50)	164.76	21.15
	120	Ethanol	94.98	30.92
	120	Water	99.42	32.53
500 W	30	Ethanol	165.23	21.68
	30	Water	177.24	15.07
	60	Ethanol-Water (50-50)	200.63	14.59
	90	Ethanol-Water (50-50)	184.56	14.84
750 W	30	Ethanol	186.25	16.51
	30	Water	195.68	15.02
	60	Ethanol-Water (50-50)	207.72	13.20
	90	Ethanol-Water (50-50)	182.34	14.38
1000 W	30	Ethanol	165.54	84.03
	30	Water	187.74	16.41
	60	Ethanol-Water (50-50)	163.32	22.15
	90	Ethanol-Water (50-50)	79.80	65.96

Based on MAE result, it is found that there is good correlation between phenolic content and antioxidant activity at EC50 (DPPH Value). Thus, the pineapple skin (peel) waste could be the excellent source of antioxidant, which is environmental friendly and renewable as compression to the commercial antioxidant.

Ultrasonic Assisted Extraction

Since, the ultrasonic assisted extraction also considered as a green extraction technology like the MAE, it requires less time and less solvent for the extraction and the extraction yield is also high. UAE is very efficiently extract phenolic compound from agro waste like pineapple waste. It is one of the simplest extraction technique because it's require only an ultrasonic bath which is again considered as a common laboratory equipment (Garcia-Salas P et al.) Principle of this technique based on the cavitation which is generated by the cycle of compression and expansion associated with the ultrasound passes to the medium. Usually 20 kHz-100 MHz frequency is used in ultrasonic technique.

This experiment can perform with the fresh sample. In the case of pineapple waste fresh peel directly use for the experiment. Sheng-Hui Liu et al is performed the experiment with the 5gm of fresh peel of pineapple and varies the extraction time 15, 30, 45, 60 and 75 min in 50ml of 70% ethanol. Ethanol concentration also varies from 50, 60, 70, 80 and 90% for 30 min.

For total phenolic content the DPPH radical scavenging activity test along with the ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) scavenging activity test is also perform for the confirmation of TPC. ABTS is same as DPPH having the same functionality, and also showed directly proportion to reduce the colour when antioxidant concentration is high.

0.1 mg/mL Ascorbic acid (Vc) was used as reference in radical scavenging ability evaluation and the result of both DPPH and ABTS v/s Vc confirm the pineapple peel is good source of phenolic content. Fig -3 and 4

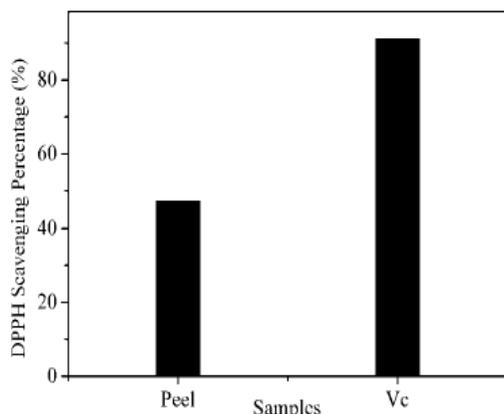


Figure 3: DPPH scavenging abilities of pineapple peel extract and Vc.

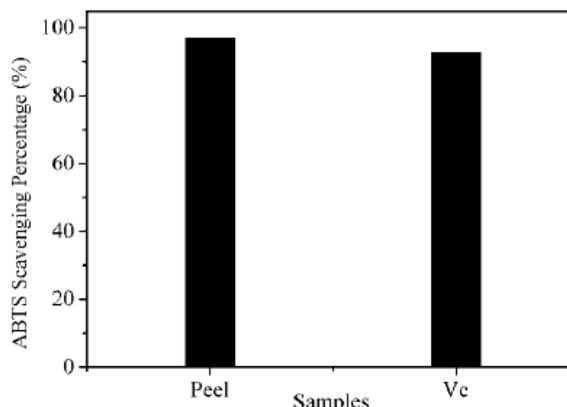


Figure 4 : ABTS scavenging abilities of pineapple peel extract and Vc.

Therefore, the conclusion of the study is pineapple peel showing excellent antioxidant abilities and research here confirm that pineapple peel will be used as natural and easily available sources of antioxidants and it also has huge potential in new application for the waste produced by pineapple processing

ADVANTAGES / DISADVANTAGES OF BOTH THE TECHNIQUE

Both the technique is having their own advantages or disadvantages mentioned as table 3

Table 3: Advantages and Disadvantages of MEA and UAE

Technique	Advantages	Disadvantages
Microwave Assisted Extraction (MAE)	▪ Fast extraction	▪ High equipment cost
	▪ Low solvent consumption	▪ Filtration required
	▪ High extraction yields	▪ Very poor efficiency for volatile compounds
Ultrasonic Assisted Extraction (UAE)	▪ High extraction efficiency	▪ Filtration required
	▪ Fast and selective extraction	▪ Lack of uniformity in the distribution of ultrasound energy
	▪ Low equipment cost	▪ Potential change in the constitutive molecules
	▪ Low operating temperature	

CONCLUSION

Unknowingly or poor knowledge of waste management, lots of essential compound like naturally occurring polyphenol, organic compound and other are not utilised properly. One of such waste is generated from pineapple waste, which has approx. 50% of total fruit. Pineapple waste consist of crown, skin or peel and core, and each portion of waste has a huge potential in term of different bioactive compound present in it. Different study also confirm that Pineapple skin waste is a good natural source of polyphenol, the total phenolic content is ranging about 7.97 ± 0.63 to 10.62 ± 0.37 mgGAE/g dw. These polyphenols extracted by using non-conventional method which is also call green extraction technique because it requires less solvent and time. Two familiar green extraction technique i.e Microwave assisted extraction and Ultrasonic assisted extraction also confirm that the pineapple skin is an excellent source of polyphenolic content. Polyphenolic content has

immense potential application in new or different industries i.e food industries, pharmaceutical industries, therapeutic industries etc.

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