Green Process Valorization of Citrus Peel Waste: Hydroalcoholic Extraction, Phytochemical Fingerprinting, and Antioxidant Performance

Mohammed ElAmin SAID[1], Khedidja BENOUIS[1], Souad BELHIA[2], Soufiane GUELLA[1], Yassine KHALFI[1]
Anes Ghazi[1], Sid Ahmed El Khalil AHED MESSAOUD[1], Kaoutar SI AFIF[1].

[1]Laboratory of Process Engineering, Materials, and Environment, Faculty of Technology, Djillali Liabes University, P.O. Box 89, Sidi Bel Abbes 22000, Algeria.
[2]Laboratory of Evolutionary Engeneering and Distributed Information System (EEDIS), Department of Computer Science, Exacte Sciences Faculty, Djillali liabes University, Sidi Bel-Abbes, Algeria.

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Abstract

This study explores the green valorization of citrus waste peels (orange (*Citrus sinensis*), mandarin (*Citrus reticulata*) and lemon (*Citrus limon*)) as renewable sources of natural antioxidants with environmental relevance. Hydroalcoholic extracts were prepared using three conventional, low-impact extraction methods (maceration, infusion and decoction), and evaluated for their total polyphenol content (TPC), total flavonoid content (TFC), condensed tannins, and antioxidant capacity using DPPH radical scavenging and ferrous ion chelation (FIC) assays. Results showed that extraction method and citrus species had a highly significant effect on all phytochemical parameters ($P < 0.05$). Decoction was the most efficient technique, yielding the highest levels of TPC, TFC and condensed tannins in all peels, with lemon consistently outperforming mandarin and orange. Maceration gave intermediate values, while infusion produced the lowest, though still appreciable, phytochemical contents. In the DPPH assay, lemon peel extract exhibited the strongest antioxidant activity (IC_{50} = 67 µg/mL), followed by mandarin and orange, with lemon displaying comparable activity to ascorbic acid and slightly higher activity than catechin. In the FIC assay, lemon and mandarin extracts showed very high chelating capacities at 5 mg/mL, approaching that of EDTA, and maintained superior activity over orange across all concentrations. The results demonstrate that citrus peels, particularly lemon, are rich, underutilized sources of bioactive compounds with strong radical-scavenging and metal-chelating properties. These findings highlight the potential of simple, scalable extraction processes to convert citrus processing and post-consumer waste into high-value antioxidant ingredients for food, cosmetic, pharmaceutical and environmental applications, contributing directly to circular bioeconomy and sustainable waste management strategies.

Keywords: Citrus peel, Phytochemical profiling, Antioxidant activity, Agro-industrial waste, DPPH, FIC.

1. INTRODUCTION

Citrus fruits are among the most widely cultivated crops worldwide, generating more than 120 million tons annually, with peels accounting for nearly one-third of the total biomass [1],[2]. This massive production inevitably leads to large quantities of organic residues that often remain underutilized or are discarded as waste, contributing to environmental pressures such as uncontrolled fermentation, methane emissions, leachate generation, and the depletion of available landfill space. In regions where agro-industrial waste management systems are limited, citrus residues become a significant source of localized pollution, underscoring the urgent need to promote sustainable valorization pathways that transform these residues into valuable bioresources [3],[4]. Such strategies align with global priorities in circular bioeconomy, environmental sustainability, and the transition toward low-carbon production systems.

Citrus peels are known to be exceptionally rich in bioactive compounds, particularly polyphenols, flavonoids, condensed tannins, limonoids, carotenoids, and essential oils, all of which exhibit demonstrable antioxidant, antimicrobial, and anti-inflammatory properties [5],[6]. The chemical richness of citrus waste makes it an attractive candidate for the development of natural antioxidants capable of replacing synthetic additives, whose toxicity and environmental persistence have raised considerable concerns in recent years [7],[8]. From an environmental science perspective, the recovery of these compounds presents a dual benefit: it mitigates the pollution associated with biomass disposal while supplying renewable, biodegradable molecules for use in food preservation, pharmaceuticals, cosmetics, and eco-friendly industrial technologies. This approach represents a core principle of green chemistry, which emphasizes the extraction of high-value compounds from renewable biomass with minimal environmental impact.

Over the last decade, growing interest in phytochemical valorization has also been supported by progress in analytical chemistry and environmental technologies. Studies on Mediterranean aromatic plants, particularly *Artemisia* species, have demonstrated how plant-derived molecules can be efficiently characterized and valorized using advanced techniques such as GC–MS, HPLC, enantiomeric analysis, and vibrational circular dichroism (VCD). These works revealed strong antioxidant and antimicrobial properties and emphasized the importance of stereochemistry in natural product bioactivity [9]-[11]. More recently, natural extracts have been successfully incorporated into green nanotechnology. Several studies, including those conducted by Said *et al.*, show that plant extracts—including citrus peels—can act as effective reducing and stabilizing agents in the synthesis of eco-friendly metallic nanoparticles with catalytic and antibacterial properties [12]. These findings reinforce the environmental value of phytochemical resources as multifunctional agents in pollution mitigation and sustainable material production.

Although citrus peels have been studied for their bioactivity, there remains a notable gap regarding the comparative analysis of extraction methods and their influence on phytochemical recovery within an environmental valorization framework. Extraction efficiency is a critical determinant of both the chemical composition and functional antioxidant performance of the resulting extracts. Temperature, solvent polarity, extraction time, and matrix structure all play essential roles in determining the stability and extractability of phenolic compounds [13],[14]. Traditional extraction processes such as maceration, infusion, and decoction remain widely used due to their simplicity, low cost, and low environmental footprint. In parallel, advanced green extraction techniques, such as ultrasound-assisted extraction, microwave processing, and natural deep eutectic solvents (NADES), have emerged as promising eco-innovative alternatives for optimal recovery of phenolic compounds from citrus biomass [15],[16]. However, the environmental sciences community still lacks comparative studies that focus simultaneously on extraction performance, antioxidant capacity, and the ecological significance of valorizing citrus peel waste.

In this context, the present study aims to contribute to environmental sustainability by investigating the green valorization of citrus waste peels, orange (*Citrus sinensis*), mandarin (*Citrus reticulata*), and lemon (*Citrus limon*), through phytochemical profiling and antioxidant analysis of hydroalcoholic extracts obtained via maceration, infusion, and decoction. Quantification of polyphenols, flavonoids, and condensed tannins is combined with two complementary antioxidant assays, DPPH radical scavenging and ferrous ion chelation, to provide a multidimensional evaluation of the antioxidant potential of these extracts. By comparing extraction techniques and linking them to both chemical and functional outcomes, this study offers environmentally relevant insights into the optimal valorization of citrus biomass, supporting waste reduction, resource recovery, and the development of natural antioxidants for sustainable applications.

2. MATERIALS AND METHODS

2.1. Plant Material and Sample Preparation

Fresh citrus peels (orange, mandarin, and lemon) were collected daily from a local restaurant in Sidi Bel Abbes, Algeria, where they represent a consistent source of post-consumer food waste. Such establishments generate substantial quantities of citrus residues from juice preparation and food service activities, making them a relevant and representative source for environmental valorization studies, as highlighted in recent circular economy research. After collection, peels were washed, air-dried, and stored under dark conditions until extraction.

2.2. Chemicals and Reagents

All chemicals used were of analytical grade, including ethanol (80%), Folin–Ciocalteu reagent, sodium carbonate, aluminum chloride, vanillin, HCl, NaOH, DPPH, ferrozine, $FeSO_4$, catechin, gallic acid, ascorbic acid, and EDTA. Solutions were freshly prepared prior to analysis.

2.3. Extraction Procedures

Three hydroalcoholic extraction methods were applied to evaluate their efficiency in recovering phytochemicals from citrus peels.

2.3.1. Maceration

Maceration was performed following standardized hydroalcoholic extraction protocols. Five grams of finely cut citrus peel were immersed in 100 mL of 80% ethanol and kept at room temperature for 72 h with constant agitation to enhance solvent diffusion and improve mass transfer. To avoid solvent saturation and maintain extraction efficiency, the ethanol was renewed every 24 h. After extraction, the mixture was filtered through Whatman No. 1 filter paper, and the filtrates were stored at 4 °C until analysis.

This method is commonly applied for the extraction of polyphenols and flavonoids due to its ability to preserve thermolabile compounds and minimize oxidative degradation [17]. Studies comparing maceration with thermal methods have shown that it yields moderate to high levels of bioactives, making it a reference technique for low-energy, green extraction [18]. Optimization studies indicate that solvent concentration, contact time, and agitation significantly influence extraction yield [19].

2.3.2. Infusion

Infusion was performed by adding five grams of citrus peel to 100 mL of preheated 80% ethanol maintained at 80 °C. The mixture was allowed to steep for 30 minutes before cooling and filtration. This approach allows rapid extraction of moderately heat-stable phenolics and flavonoids while limiting prolonged thermal degradation.

Infusion is often considered an intermediate-intensity extraction method, and comparative studies have shown that it yields lower phenolic content than decoction but may outperform maceration for certain heat-stable compounds [17],[18]. Temperature and steeping duration are the main variables influencing extraction efficiency, and several optimization studies highlight the importance of maintaining controlled heating to preserve antioxidant potential [20],[21].

2.3.3. Decoction

Decoction was carried out by boiling five grams of citrus peel in 100 mL of 80% ethanol for 10 minutes. After cooling, extracts were filtered and stored at 4 °C. Decoction is known to promote the release of heat-stable phenolics, condensed tannins, and glycosylated flavonoids by increasing cell wall disruption and improving solvent penetration.

Numerous studies confirm that decoction yields significantly higher levels of polyphenols, tannins, and antioxidants compared to maceration or infusion, due to thermal depolymerization of proanthocyanidins and weakening of polysaccharide–polyphenol interactions [17],[22]. Optimization research shows that boiling temperature, extraction duration, and solvent polarity are critical factors determining extraction efficiency [13],[20].

2.4. Phytochemical Quantification

2.4.1. Total Polyphenol Content (TPC)

Total phenolic content was determined using the Folin–Ciocalteu method, where phenolic compounds reduce the phosphomolybdic–phosphotungstic reagents to produce blue oxides measurable at 765 nm [23]. For this assay, 200 µL of extract were mixed with 1 mL of diluted Folin reagent and 800 µL of sodium carbonate (7.5%), then incubated for 30 minutes in the dark before reading the absorbance at 765 nm. A calibration curve using gallic acid was used to express results as mg gallic acid equivalents per 100 gram of extract (mg GAE/100 g).

2.4.2. Total Flavonoid Content (TFC)

Total flavonoids were quantified according to the aluminum chloride method described by Zhishen *et al.* based on the formation of flavonoid–$AlCl_3$ complexes producing a yellow chromophore measurable at 510 nm [24]. A mixture of extract, distilled water, sodium nitrite, aluminum chloride, and sodium hydroxide was prepared sequentially, and after incubation the absorbance at 510 nm was recorded. Flavonoid concentrations were expressed as mg catechin equivalent per 100 gram of extract (mg CE/100 g).

2.4.3. Condensed Tannins

Condensed tannins were quantified using the vanillin–HCl method described by Broadhurst & Jones and Heimler *et al.*, where tannin units react with vanillin in acidic medium to produce a red chromophore with absorbance at 550 nm [22],[25]. For this assay, extract was mixed with vanillin solution and concentrated HCl, incubated for 20 minutes, and the absorbance recorded at 550 nm. Results were expressed as catechin equivalents per 100 gram of extract (mg CE/100g).

2.5. Antioxidant activity

2.5.1. DPPH Radical Scavenging Activity

The antioxidant activity of citrus peel extracts was assessed using the DPPH free radical scavenging method, in which the stable purple chromogenic DPPH• radical is reduced by hydrogen-donating antioxidants into the corresponding pale-yellow hydrazine form, resulting in a measurable decrease in absorbance at 515 nm. The assay was conducted by preparing extract concentrations of 2000, 1000, 500, 250, 125, 62.5, 31.25 and 15.62 µg/mL, along with positive controls including ascorbic acid, gallic acid and catechin. A volume of 50 µL of each concentration was mixed with 1950 µL of methanolic DPPH solution (25 mg/L), and the mixture was incubated in the dark for 30 minutes at room temperature before absorbance measurement at 515 nm, following protocols widely used in natural antioxidant studies [26], [27]. The radical scavenging activity (RSA) was calculated using the following equation:

$$RSA\ (\%) = \frac{A_c - A_s}{A_c} \times 100$$

where A_c is the absorbance of the control sample (DPPH solution), and A_s is the absorbance in the presence of extract or control. Antioxidant effectiveness was expressed as IC_{50}, defined as the concentration required to inhibit 50% of the DPPH radical and determined graphically from the graph plotting scavenging percentage against test sample concentration (µg/mL). DPPH radicals decrease significantly upon exposure to radical remover.

2.5.2. Iron Chelating Activity (FIC Assay)

The ferrous ion chelating activity of citrus peel extracts was evaluated according to an adapted version of the method described by Gülçin, which assesses the extract's ability to disrupt the Fe^{2+}–ferrozine complex by competing with ferrozine for iron binding [28]. In this assay, 1 mL of $FeSO_4$ solution (0.1 mM) was combined with 1 mL of extract at different concentrations, followed by the addition of 1 mL of ferrozine solution (0.25 mM). The reaction mixtures were incubated for 10 minutes at room temperature, after which their absorbance was recorded at 562 nm. Ascorbic acid, catechin, gallic acid and EDTA served as positive controls due to their well-established metal binding capabilities. The percentage of chelation was determined using the formula:

$$FIC\ (\%) = \frac{A_0 - A_s}{A_0} \times 100$$

where A_0 is the absorbance of the negative control (methanol, $FeSO_4$ and ferrozine) and A_s is the absorbance in the presence of extract or control. A higher percentage indicates a stronger ability to chelate ferrous ions, a mechanism of major environmental interest because it prevents Fe^{2+}-mediated oxidative reactions and metal-catalyzed radical formation [28].

2.6. Statistical Analysis

Statistical analyses were performed using JASP (version 0.95.4). One-way ANOVA followed by Tukey's post-hoc multiple comparison test was applied to evaluate significant differences between extract samples and reference antioxidants. All measurements were carried out in triplicate across three independent experiments, and results are expressed as mean ± standard deviation (SD). Statistical significance was established at $p < 0.05$, in accordance with conventional analytical standards.

3. RESULTATS AND DISCUTIONS

3.1. Phytochemical Composition of Citrus Peel Extracts

3.1.1. Total Phenolic Content (TPC)

Figure 1 illustrates the total phenolic content of orange, mandarin, and lemon peel extracts obtained through maceration, infusion, and decoction.

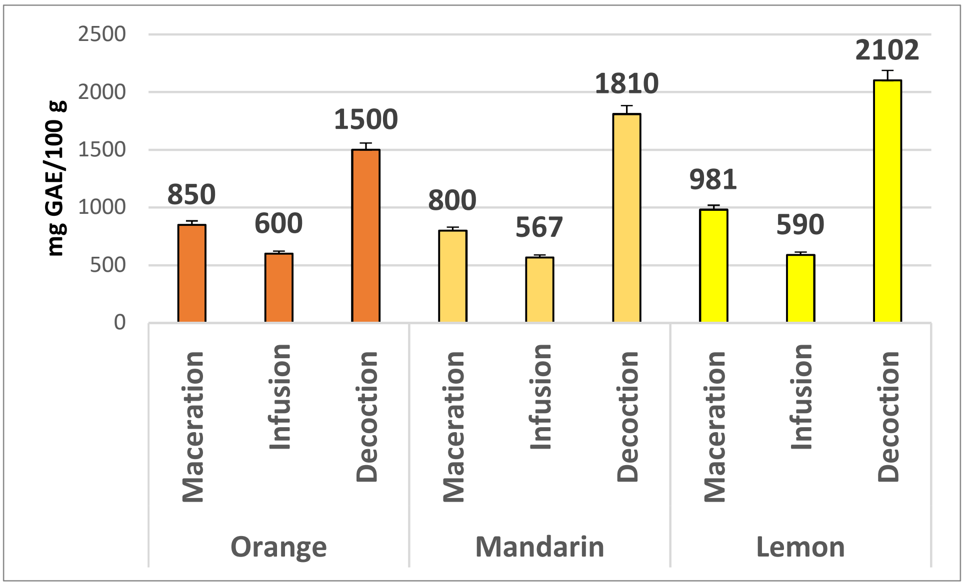

Figure 1 : Total phenolic content of citrus peel extracts.

Decoction emerged as the most efficient extraction technique, yielding exceptionally high phenolic levels in all samples. The lemon decoction exhibited the highest TPC (2102 mg GAE/ 100g), followed by mandarin (1810 mg GAE/100 g) and orange (1500 mg GAE/100 g). Tukey's post-hoc test showed that the TPC values of decoction extracts were significantly higher than those of maceration and infusion for all three citrus species ($P < 0.05$). This superior performance is largely attributed to the effect of elevated temperatures, which promote cell wall disruption, enhance phenolic solubilization, and facilitate the release of bound compounds from the plant matrix. These findings agree with recent studies demonstrating that thermal extraction significantly improves phenolic recovery in citrus fruits [29]-[31]. Although less efficient than decoction, maceration produced remarkably high phenolic contents, particularly for lemon (981 mg GAE/100 g), followed by orange (850 mg GAE/100 g) and mandarin (800 mg GAE/100 g). ANOVA confirmed a significant difference between maceration extracts of lemon and the other species ($P < 0.05$), reflecting the naturally higher phenolic richness of *Citrus limon*. These values are considerably higher than those reported in earlier studies, where macerated citrus peel extracts often contain less than 500 mg GAE/100 g [32],[33]. Such enhanced extraction may be attributed to the optimized hydroalcoholic solvent system and the phytochemical richness of the local varieties used in this study.

Infusion yielded the lowest TPC values, reflecting moderate temperature and short extraction time. The differences between infusion and maceration for each citrus species were statistically significant ($P < 0.05$), confirming that infusion is less effective for recovering bound phenolics. Nevertheless, infusion extracts, especially lemon (590 mg GAE/100 g), still exhibited appreciable phenolic levels, supporting the inherently high antioxidant potential of citrus by-products.

Overall, a clear and statistically supported trend was observed across all methods: lemon > mandarin > orange. This hierarchy aligns with previous findings reporting that *Citrus limon* naturally contains higher levels of phenolic acids and flavanones [7],[34]. These species-specific differences are likely associated with distinct metabolic pathways, peel morphology, and environmental adaptation mechanisms.

3.1.2. Total Flavonoid Content (TFC)

Figure 2 presents the total flavonoid content of citrus peel extracts obtained using maceration, infusion, and decoction.

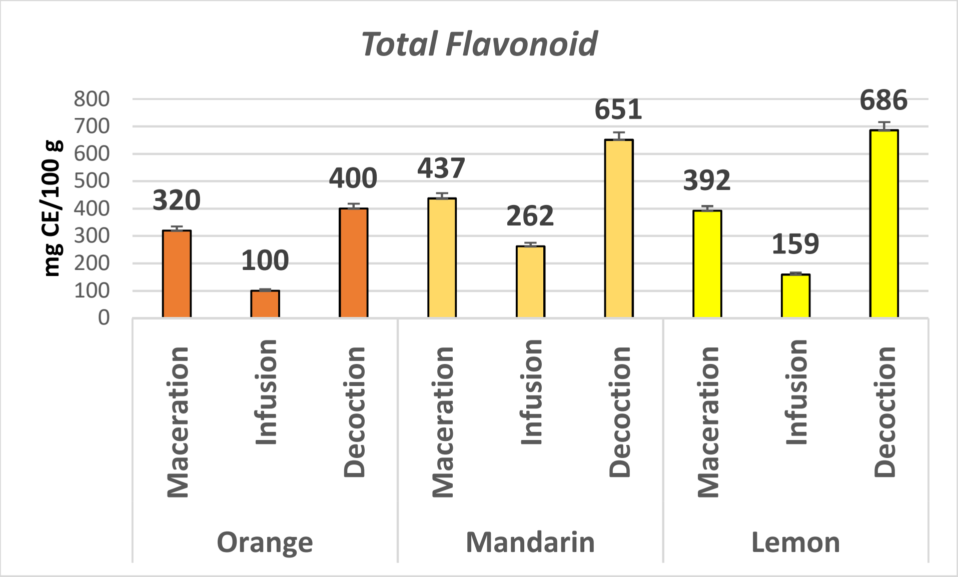

Figure 2 : Total flavonoid content of citrus peel extracts.

As observed for total phenolics, flavonoid recovery was strongly affected by the extraction technique, with decoction yielding the highest concentrations across all citrus species. Decoction extracts exhibited flavonoid contents of 686 mg CE/100 g in lemon, 651 mg CE/100 g in mandarin, and 400 mg CE/100 g in orange. Tukey's post-hoc test confirmed that decoction extracts were significantly higher than maceration and infusion for all species ($P < 0.05$). This aligns with previous studies showing that thermal extraction enhances the release of glycosylated flavonoids such as hesperidin, naringin, and eriocitrin due to improved solvent penetration and disruption of polysaccharide–flavonoid interactions [35],[36]. Maceration also produced noteworthy flavonoid levels, 437 mg CE/100 g in mandarin, 392 mg CE/100 g in lemon, and 320 mg CE/100 g in orange. These values were significantly lower than those obtained by decoction ($P < 0.05$) but significantly higher than infusion ($P < 0.05$), demonstrating the intermediate efficiency of this method. The higher TFC in mandarin and lemon compared to orange was statistically significant ($P < 0.05$) and suggests inherent varietal differences, consistent with literature showing that *Citrus reticulata* and *Citrus limon* possess higher concentrations of flavanone glycosides than *Citrus sinensis* [37]. Compared with earlier studies where maceration typically yields only 150–300 mg CE/100 g, the values obtained here reflect the richness of local citrus peels and the effectiveness of the hydroalcoholic solvent system.

Infusion resulted in the lowest TFC values, ranging from 100 mg CE/100 g in orange to 262 mg CE/100 g in mandarin and 159 mg CE/100 g in lemon. These values were significantly lower than both maceration and decoction ($P < 0.05$), confirming that moderate heating and short extraction time limit flavonoid release. However, despite lower yields, infusion still recovered meaningful levels of bioactive compounds, supporting the robustness of citrus flavonoids even under milder conditions.

Overall, the trend lemon > mandarin > orange was consistently observed across extraction methods, and all differences between species were statistically significant ($P < 0.05$). This hierarchy reinforces earlier findings that *Citrus limon* and *Citrus reticulata* possess richer flavonoid profiles than *Citrus sinensis*. The exceptionally high values obtained by decoction underscore the strong thermal stability of major citrus flavonoids, making high-temperature extraction particularly effective for their recovery [38],[39].

3.1.3. Condensed Tannins

Figure 3 shows the condensed tannin content of citrus peel extracts obtained through maceration, infusion, and decoction.

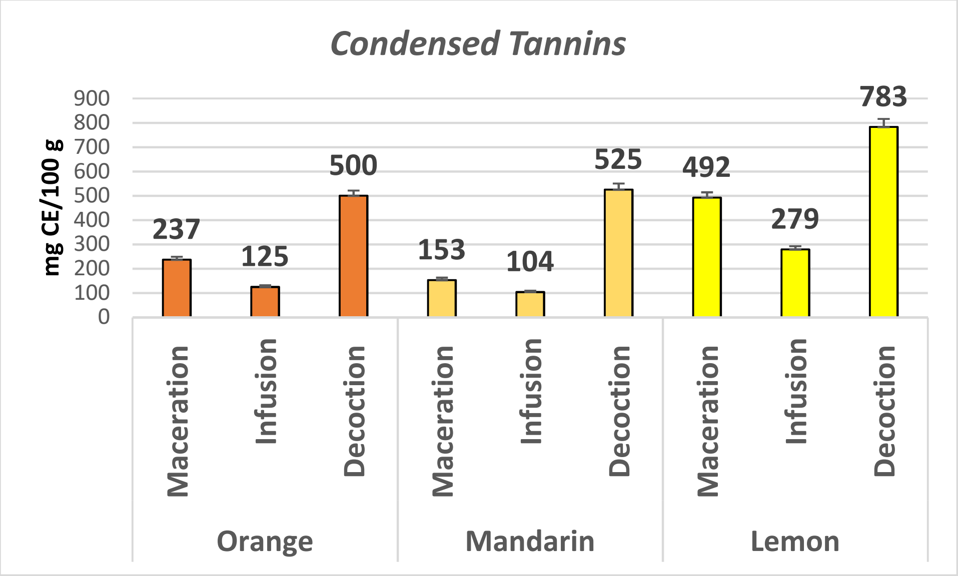

Figure 3 : Condensed tannin content of citrus peel extracts.

As with phenolics and flavonoids, decoction consistently produced the highest levels of condensed tannins. The highest concentration was recorded for lemon (783 mg CE/100 g), followed by mandarin (525 mg CE/100 g) and orange (500 mg CE/100 g). Tukey's post-hoc test confirmed that tannin contents obtained through decoction were significantly higher than those obtained by maceration and infusion for all species ($P < 0.05$). This enhanced extraction efficiency reflects the thermal sensitivity of proanthocyanidins, whose depolymerization and release are strongly favored at elevated temperatures. Similar observations were reported by Heimler *et al.*, who demonstrated that heating promotes tannin solubilization by weakening cell wall–polyphenol interactions [40].

Maceration produced moderate condensed tannin levels: 492 mg CE/100 g in lemon**,** 237 mg CE/100 g in orange, and 153 mg CE/100 g in mandarin. These differences between species were statistically significant ($P < 0.05$), reflecting natural variability in tannin composition across citrus taxa. The particularly high value observed in lemon agrees with studies reporting that *Citrus limon* peels contain higher levels of polymerized proanthocyanidins, which contribute to stronger antioxidant and astringent characteristics [41],[42]. The lower tannin concentration in mandarin is consistent with its known lower abundance of polymerized flavan-3-ols.

Infusion yielded the lowest tannin contents, 104 mg CE/100 g in mandarin**,** 125 mg CE/100 g in orange**,** and 279 mg CE/100 g in lemon, and these values were significantly lower than those obtained by maceration and decoction ($P < 0.05$). This result is expected, as condensed tannins, especially high-molecular-weight proanthocyanidins, have limited solubility under moderate temperature conditions and require stronger extraction forces or prolonged heating for efficient recovery.

Across all extraction techniques, lemon peel consistently displayed the highest tannin levels, a trend that was statistically significant ($P < 0.05$) and supports its classification as an exceptionally rich source of antioxidant phytochemicals. The strong performance of decoction for tannin extraction aligns with recent studies demonstrating that elevated temperatures improve both diffusion and desorption of tannin molecules from citrus flavedo and albedo tissues [43].

Overall, the pattern lemon > mandarin > orange highlights species-specific phytochemical profiles and reinforces the potential of citrus peels, particularly lemon, as valuable raw materials for antioxidant-rich formulations, nutraceuticals, and sustainable valorization strategies.

3.2. Antioxidant activity

3.2.1. DPPH Radical Scavenging Activity

The DPPH radical scavenging assay revealed clear differences in antioxidant capacity among the citrus peel extracts (Table 1).

Table 1 : Half maximal DPPH radical scavenging concentration of extracts and controls

Sample	Orange	Mandarin	Lemon	Catechin	Gallic acid	Ascorbic acid
IC_{50} (µg/mL)	116 ± 7.5	87 ± 5.2	67 ± 4.1	85 ± 3.8	34 ± 2.1	76 ± 4.6

The lemon extract showed the strongest activity with an IC_{50} value of 67 ± 4.1 µg/mL, followed by mandarin (87 ± 5.2 µg/mL) and orange (116 ± 7.5 µg/mL). Statistical analysis confirmed that the effect of citrus species on DPPH inhibition was highly significant ($P < 0.05$). Tukey's post-hoc test showed that lemon extract exhibited significantly stronger activity than mandarin ($P < 0.05$) and orange ($P < 0.05$), while mandarin was also significantly more active than orange ($P < 0.05$). These results are consistent with previous findings indicating that *Citrus limon* possesses higher concentrations of flavanones and phenolic acids that enhance radical-scavenging efficiency [5],[44],[45].

When comparing citrus extracts with the antioxidant standards, the results showed that gallic acid (34 ± 2.1 µg/mL) was significantly more potent than all citrus samples ($P < 0.05$), confirming its well-known strong electron-donating capacity. Lemon extract did not differ significantly from ascorbic acid (76 ± 4.6 µg/mL, $P > 0.05$), indicating comparable antioxidant performance. However, lemon extract exhibited slightly stronger activity than catechin (85 ± 3.8 µg/mL), with the difference approaching statistical significance ($P < 0.05$). Mandarin extract showed a level of activity similar to that of catechin ($P > 0.05$) but remained significantly weaker than gallic acid ($P < 0.05$). Orange extract, with the highest IC_{50} value, was significantly less active than all standards ($P < 0.05$).

Overall, the DPPH results demonstrate that citrus peels, particularly lemon and mandarin, exhibit substantial antioxidant power, comparable in some cases to classical phenolic standards. These findings highlight their potential for incorporation into natural antioxidant formulations, food preservation systems, and eco-friendly products aligned with green chemistry principles.

3.2.2. Iron Chelating Activity (FIC Assay)

Figure 4 presents the chelating activity of citrus peel extracts at three concentrations (5, 2.5, and 1.75 mg/mL).

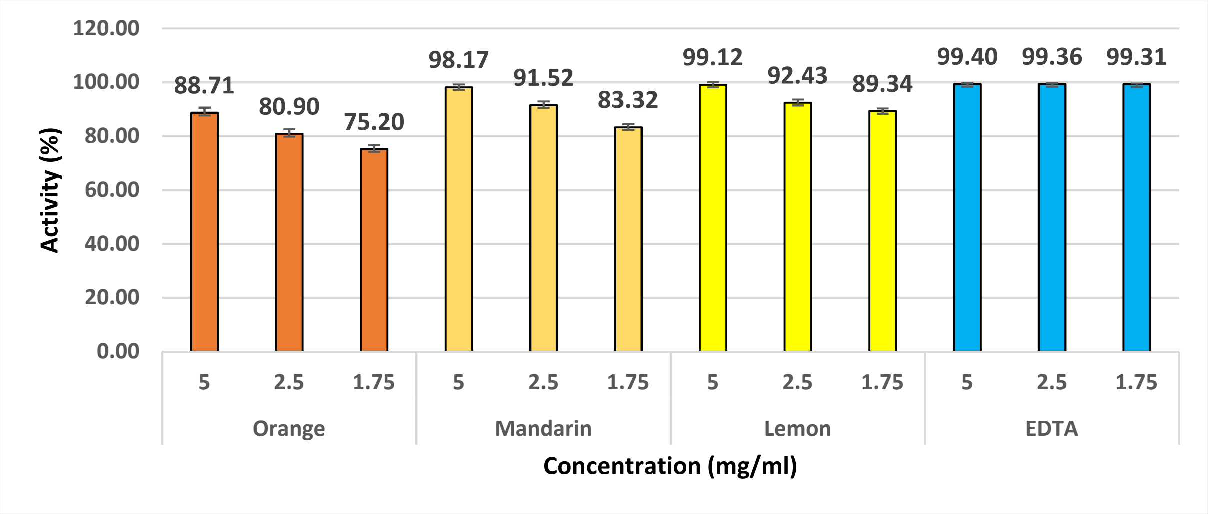

Figure 4 : Chelating activity of citrus peel extracts

The ferrous ion chelation assay revealed that all citrus extracts exhibited strong metal-binding activity, with chelation increasing proportionally with concentration. Lemon peel extract consistently showed the highest activity at all levels (99.12%, 92.43%, and 89.34% at 5, 2.5, and 1.75 mg/mL, respectively), followed by mandarin and orange. At 5 mg/mL, the chelating performance of lemon (99.12%) and mandarin (98.17%) approached that of EDTA (99.40%), the synthetic reference chelator. ANOVA demonstrated a highly significant effect of citrus species on chelating activity across all concentrations ($P < 0.05$). Tukey's post-hoc analysis confirmed that both lemon and mandarin extracts possessed significantly greater activity than orange at 5 mg/mL ($P < 0.05$), whereas the difference between lemon and mandarin was not statistically significant ($P = 0.214$), indicating comparable chelating strength at higher concentrations. At lower concentrations, however, lemon remained significantly more active than mandarin ($P < 0.05$) and orange ($P < 0.05$), while mandarin retained significantly stronger activity than orange ($P < 0.05$), maintaining the consistent hierarchy lemon > mandarin > orange.

These findings are fully aligned with previous reports describing citrus peels, particularly lemon, as rich sources of metal-chelating polyphenols. Studies by Ghasemi *et al*. demonstrated that *Citrus limon* peels contain high levels of phenolic acids and flavanones capable of forming stable complexes with transition metals, resulting in chelating activities comparable to synthetic agents [46]. Similarly, Goulas and Manganaris reported that lemon extracts possess superior Fe^{2+}-chelating power relative to orange and mandarin, a trend reflected in the present work [47]. The strong performance of decoction-derived extracts is also consistent with observations by Heimler *et al*., who found that heating enhances the solubilization of polymerized proanthocyanidins and other chelating-active phenolics by weakening cell wall–polyphenol interactions [22]. More recent studies support this behavior, showing that elevated temperature improves both diffusion and desorption processes, facilitating the release of chelating compounds from citrus tissues [48].

Although EDTA exhibited the highest and most stable chelating performance, the absence of a significant difference between EDTA and the lemon extract at 5 mg/mL ($P > 0.05$) is noteworthy. Comparable observations were reported by many studies, who demonstrated that polyphenol-rich citrus extracts can approach the efficiency of synthetic chelators under optimized extraction conditions [49]. This remarkable capability highlights the relevance of citrus peel valorization for environmental applications, as natural chelators derived from agri-food waste offer a sustainable alternative for reducing metal-induced oxidative stress, supporting green corrosion inhibition, and enhancing eco-friendly formulations.

4. Conclusion

This work demonstrates that citrus processing and post-consumer peels constitute a rich, underexploited source of phytochemicals with strong antioxidant potential. Among the three green extraction methods evaluated, decoction systematically yielded the highest levels of total polyphenols, flavonoids and condensed tannins, followed by maceration, while infusion, although less efficient, still provided appreciable amounts of bioactive compounds. In all cases, lemon peels showed the greatest phytochemical richness, confirming their prominence as a particularly valuable citrus by-product.

The antioxidant assays further reinforced these findings. Lemon and mandarin extracts exhibited strong DPPH radical scavenging activity, with lemon presenting IC_{50} values comparable to ascorbic acid and close to catechin. In parallel, ferrous ion chelation tests revealed that lemon and mandarin extracts can approach the chelating capacity of EDTA at higher concentrations, highlighting their ability to sequester transition metals and potentially limit metal-driven oxidative processes. Together, these results underscore the dual functional role of citrus peel extracts as both radical scavengers and metal chelators.

From an environmental science perspective, the study confirms that simple, low-cost and scalable extraction processes can transform citrus peel waste into high-value antioxidant ingredients suitable for food preservation, cosmetic and pharmaceutical formulations, as well as eco-friendly materials and potential applications in pollution mitigation. By integrating waste reduction, resource recovery and the production of natural additives, this work directly contributes to the principles of green chemistry and circular bioeconomy.

Future research should focus on scaling up the most promising extraction conditions, characterizing individual bioactive molecules in greater detail, and assessing the performance of citrus peel extracts in real formulation systems (e.g. food, packaging, or water treatment). Such efforts will help bridge the gap between laboratory evidence and industrial implementation, consolidating citrus peel valorization as a practical tool for sustainable environmental management.

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REFERENCES

[1] Zema, D. A., Calabrò, P. S., Folino, A., Tamburino, V., Zappia, G., and Zimbone, S. M., 2018, "Valorisation of Citrus Processing Waste: A Review," *Waste Management*, 80, pp. 252–273.

[2] Morales, J., Medina, A., and Bermejo, A., 2025, "Sustainable Extraction of Flavonoids from Citrus Waste: A Fast and Simple Approach with UHPLC-PDA ESI-MS Characterization," *Sci*, 7(4), p. 156.

[3] Mirabella, N., Castellani, V., and Sala, S., 2014, "Current Options for the Valorization of Food Manufacturing Waste: A Review," *Journal of Cleaner Production*, 65, pp. 28–41.

[4] Lizundia, E., Luzi, F., and Puglia, D., 2022, "Organic Waste Valorisation Towards Circular and Sustainable Biocomposites," *Green Chemistry*, 24(14), pp. 5429–5459.

[5] Ashraf, H., Iahtisham-Ul-Haq, Butt, M. S., Nayik, G. A., Ramniwas, S., Damto, T., Alharbi, S. A., and Ansari, M. J., 2024, "Phytochemical and Antioxidant Profile of Citrus Peel Extracts in Relation to Different Extraction Parameters," *International Journal of Food Properties*, 27(1), pp. 286–299.

[6] Zheng, Y., Wu, Y., Wang, B., Wang, H., Zhang, Y., Wang, W., and Yu, L., 2024, "Flavonoids Analysis in Citrus Peels by UPLC-Q-TOF-MS/MS and its Antioxidant and Anti-Inflammation Activity," *Food Chemistry Advances*, 5, p. 100853.

[7] Andrade, M. A., Barbosa, C. H., Shah, M. A., Ahmad, N., Vilarinho, F., Khwaldia, K., Silva, A. S., and Ramos, F., 2023, "Citrus By-products: Valuable Source of Bioactive Compounds for Food Applications," *Antioxidants*, 12(1), p. 38.

[8] Silva, M. M., Santos, M. R., Caroço, G., Rocha, R., Justino, G., and Mira, L., 2002, "Structure–Antioxidant Activity Relationships of Flavonoids: A Re-examination," *Free Radical Research*, 36(11), pp. 1219–1227.

[9] Said, M. E.-A., Vanloot, P., Bombarda, I., Naubron, J.-V., Dahmane, E. M., Aamouche, A., Jean, M., Vanthuyne, N., Dupuy, N., and Roussel, C., 2016, "Analysis of the Major Chiral Compounds of *Artemisia herba-alba* Essential Oils Using Reconstructed VCD Spectra," *Analytica Chimica Acta*, 903, pp. 121–130.

[10] Said, M. E.-A., Bombarda, I., Naubron, J.-V., Vanloot, P., Jean, M., Cheriti, A., Dupuy, N., and Roussel, C., 2017, "Isolation of the Major Chiral Compounds from *Bubonium graveolens* Essential Oil by HPLC and Absolute Configuration Determination by VCD," *Chirality*, 29(2), pp. 70–79.

[11] Said, M., Militello, M., Saia, S., Settanni, L., Aleo, A., Mammina, C., Bombarda, I., Vanloot, P., and Dupuy, N., 2016, "*Artemisia arborescens* Essential Oil Composition, Enantiomeric Distribution, and Antimicrobial Activity," *Chemistry & Biodiversity*, 13.

[12] Hamze, Z. K., Assi, S., Mhanna, R., Bouaziz, M., Said, M. E. A., Benouis, K., Fayad, L., Younes, G. O., and El-Dakdouki, M. H., 2025, "Sustainable Preparation of Multifunctional Green Silver Nanoparticles," *Environmental Science and Pollution Research*, 32(39), pp. 22698–22718.

[13] Antony, A., and Farid, M., 2022, "Effect of Temperatures on Polyphenols During Extraction," *Applied Sciences*, 12(4), p. 2107.

[14] Almeida, P. V., Rodrigues, R. P., Slezak, R., and Quina, M. J., 2022, "Effect of Phenolic Compound Recovery from Agro-industrial Residues on Pyrolysis Performance," *Biomass Conversion and Biorefinery*, 12(10), pp. 4257–4269.

[15] Medina-Torres, N., Espinosa-Andrews, H., Trombotto, S., Ayora-Talavera, T., Patrón-Vázquez, J., González-Flores, T., Sánchez-Contreras, Á., Cuevas-Bernardino, J. C., and Pacheco, N., 2019, "Ultrasound-Assisted Extraction Optimization of Phenolic Compounds from *Citrus latifolia* Waste," *Molecules*, 24(19), p. 3541.

[16] Bairaktari, M., Konstantopoulou, S. M., Malisova, O., Gioxari, A., Stratakos, A. C., Panoutsopoulos, I. G., and Argyri, K., 2025, "Natural Deep Eutectic Solvents for Agro-Industrial By-product Valorization," *Applied Sciences*, 15(21), p. 11596.

[17] Larbi, K. S., Belmimoun, A., Meddah, B., Ouahdi, M., Maizi, Y., Touil, A. T., Ternifi, M., and Kebaili, D., 2022, "Effect of Extraction Process on Phytochemical Composition and Antioxidant Properties of *Rosmarius officinalis* and *Globularia alypum* Extracts," *South Asian Journal of Experimental Biology*, 12(3), pp. 429–437.

[18] Persic, M., Veberic, R., and Mikulic-Petkovsek, M., 2019, "Phenolic Profiles of Quince Leaf Extracts Obtained by Different Extraction Methods," *Acta Botanica Croatica*, 78(2), pp. 175–180.

[19] Riza, A., Ilyas, S., Sjamsudin, E., and Delyuzar, D., 2024, "Effect of Extraction Method and Solvent Type on Total Phenolics, Total Flavonoids and Antioxidant Activity of *Centella asiatica* Extract," *Bioscientia Medicina*, 8(1), pp. 3873–3881.

[20] Muala, W. C. B., Desobgo, Z. S. C., and Jong, N. E., 2021, "Optimization of Extraction Conditions of Phenolic Compounds from *Cymbopogon citratus*," *Heliyon*, 7(4), p. e06744.

[21] Begum, S. N., Hossain, M., Adnan, M., Rahaman, C. H., and Reza, A., 2023, "Optimization and Characterization of Phenolic Extraction and Antioxidant Activity of *Adenanthera pavonina* Bark," *Plants*, 12(22), p. 3902.

[22] Heimler, D., Isolani, L., Vignolini, P., Tombelli, S., and Romani, A., 2007, "Polyphenol Content and Antioxidative Activity in Freshly Consumed Salads," *Journal of Agricultural and Food Chemistry*, 55(5), pp. 1724–1729.

[23] Singleton, V. L., and Rossi, J. A., 1965, "Colorimetry of Total Phenolics with Phosphomolybdic-Phosphotungstic Reagents," *American Journal of Enology and Viticulture*, 16(3), pp. 144–158.

[24] Zhishen, J., Mengcheng, T., and Jianming, W., 1999, "Determination of Flavonoid Contents in Mulberry," *Food Chemistry*, 64(4), pp. 555–559.

[25] Broadhurst, R. B., and Jones, W. T., 1978, "Analysis of Condensed Tannins Using Acidified Vanillin," *Journal of the Science of Food and Agriculture*, 29(9), pp. 788–794.

[26] Brand-Williams, W., Cuvelier, M. E., and Berset, C., 1995, "Use of a Free Radical Method to Evaluate Antioxidant Activity," *LWT – Food Science and Technology*, 28(1), pp. 25–30.

[27] Ammar, R. B., Bhouri, W., Sghaier, M. B., Boubaker, J., Skandrani, I., Neffati, A., Bouhlel, I., Kilani, S., Mariotte, A.-M., Chekir-Ghedira, L., Dijoux-Franca, M.-G., and Ghedira, K., 2009, "Antioxidant and Free Radical-Scavenging Properties of Three Flavonoids," *Food Chemistry*, 116(1), pp. 258–264.

[28] Gulcin, I., and Alwasel, S. H., 2022, "Metal Ions, Metal Chelators and Metal Chelating Assay as Antioxidant Method," *Processes*, 10(1), p. 132.

[29] Xu, G., Ye, X., Chen, J., and Liu, D., 2007, "Effect of Heat Treatment on Phenolic Compounds and Antioxidant Capacity of Citrus Peel Extract," *Journal of Agricultural and Food Chemistry*, 55(2), pp. 330–335.

[30] Jeong, S.-M., Kim, S.-Y., Kim, D.-R., Jo, S.-C., Nam, K. C., Ahn, D. U., and Lee, S.-C., 2004, "Effect of Heat Treatment on the Antioxidant Activity of Citrus Peel Extracts," *Journal of Agricultural and Food Chemistry*, 52(11), pp. 3389–3393.

[31] M'hiri, N., Ioannou, I., Ghoul, M., and Mihoubi Boudhrioua, N., 2017, "Phytochemical Characteristics of Citrus Peel and Processing Effects on Phenolics," *Food Reviews International*, 33(6), pp. 587–619.

[32] Ogo, O., Hembafan, N., Amokaha, R., Jeremiah, O., and Inalegwu, B., 2024, "Characterization and Antioxidant Activity of Peel Extracts from Three Varieties of *Citrus sinensis*," *Heliyon*, 10(7), p. e28456.

[33] M'hiri, N., Ioannou, I., Ghoul, M., and Boudhrioua, N. M., 2014, "Extraction Methods of Citrus Peel Phenolic Compounds," *Food Reviews International*, 30(4), pp. 265–290.

[34] Zhu, C., Zhou, X., Long, C., Du, Y., Li, J., Yue, J., and Pan, S., 2020, "Variations of Flavonoid Composition and Antioxidant Properties among Citrus Cultivars," *Chemistry & Biodiversity*, 17(6), p. e1900690.

[35] Dadwal, V., and Gupta, M., 2023, "Recent Developments in Citrus Bioflavonoid Encapsulation," *Critical Reviews in Food Science and Nutrition*, 63(9), pp. 1187–1207.

[36] Liu, Y., Yan, N., Chen, Q., Dong, L., Li, Y., Weng, P., Wu, Z., Pan, D., Liu, L., Farag, M. A., Wang, L., and Liu, L., 2024, "Research Advances in Citrus Polyphenols," *Critical Reviews in Food Science and Nutrition*, 64(31), pp. 11493–11509.

[37] Nogata, Y., Sakamoto, K., Shiratsuchi, H., Ishii, T., Yano, M., and Ohta, H., 2006, "Flavonoid Composition of Citrus Species," *Bioscience, Biotechnology, and Biochemistry*, 70(1), pp. 178–192.

[38] Preet, G., Haj Hasan, A., Ramlagan, P., Fawdar, S., Boulle, F., and Jaspars, M., 2023, "Anti-neurodegenerating Activity and Structure–Activity Relationships of Flavonoids," *Molecules*, 28(20), p. 7188.

[39] Yu, L., Wu, Y., Liu, D., Sheng, Z., Liu, J., Chen, H., and Feng, W., 2022, "Kinetic Behavior and Stability of Polyphenol Extracts from Navel Orange Peel," *Food Science and Technology*, 42, p. e90621.

[40] Marangon, M., Vincenzi, S., Lucchetta, M., and Curioni, A., 2010, "Heating and Reduction Affect Tannin–Protein Interactions," *Analytica Chimica Acta*, 660(1), pp. 110–118.

[41] Scalbert, A., 1992, "Tannins in Woods and Their Contribution to Microbial Decay Prevention," in *Plant Polyphenols: Synthesis, Properties, Significance*, Hemingway, R. W., and Laks, P. E., eds., Springer, Boston, MA, pp. 935–952.

[42] Munir, H., Yaqoob, S., Awan, K. A., Imtiaz, A., Naveed, H., Ahmad, N., Naeem, M., Sultan, W., and Ma, Y., 2024, "Unveiling the Chemistry of Citrus Peel: Nutraceutical Potential and Therapeutic Applications," *Foods*, 13(11), p. 1681.

[43] Dias, E. C. P. P., Macedo, G. A., Camargo, G. A., Macedo, J. A., and Chiocchetti, G. M., 2024, "Effects of Extraction Processes on Phenolic Recovery and Antiglycation Activity from Green Coffee Residues," *ACS Sustainable Chemistry & Engineering*, 12(36), pp. 13464–13474.

[44] Zou, Z., Xi, W, Hu, Y., Nie, C., and Zhou, Z., 2016, "Antioxidant Activity of Citrus Fruits," *Food Chemistry*, 196, pp. 885–896.

[45] Zia-ur-Rehman, 2006, "Citrus Peel Extract – A Natural Source of Antioxidant," *Food Chemistry*, 99(3), pp. 450–454.

[46] Ghasemi, K., Ghasemi, Y., and Ebrahimzadeh, M. A., 2009, "Antioxidant Activity and Phenol and Flavonoid Contents of 13 Citrus Species Peels and Tissues," *Pakistan Journal of Pharmaceutical Sciences*, 22(3), pp. 277–281.

[47] Goulas, V., and Manganaris, G. A., 2012, "Exploring the Phytochemical Content and Antioxidant Potential of Citrus Fruits Grown in Cyprus," *Food Chemistry*, 131(1), pp. 39–47.

[48] Bezerra, F. de S., and Koblitz, M. G. B., 2025, "Extraction of Phenolic Compounds from Agro-Industrial By-products Using Natural Deep Eutectic Solvents," *Separations*, 12(6), p. 150.

[49] Borghi, S. M., and Pavanelli, W. R., 2023, "Antioxidant Compounds and Health Benefits of Citrus Fruits," *Antioxidants*, 12(8), p. 1526.