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Green extraction of lycopene and volatile compounds from *Solanum lycopersicum* (Tomato) peel and products

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ABSTRACT

The primary aim of this study is the quantitative determination of lycopene and volatile composition in tomato peel and commercial tomato products using subcritical ethanol extraction. Box- Behnken Response Surface Methodology was conducted in order to evaluate the key operational parameters of the extraction process. The priority of the current study was to determine the lycopene efficiency; however, antioxidant activity and total volatile analysis of the extracts were also further evaluated using spectroscopic and chromatographic assays. AGREE-Analytical greenness metric software was applied to evaluate the greenness of the proposed extraction process. These findings demonstrate the efficiency of the proposed procedure in achieving the highest extraction yield (6.51 mg g^{-1}) from tomato peel in the literature. The study emphasises the significance of advanced extraction technologies in converting agricultural raw material or waste into value-added products, thereby promoting the advancement of a green circular economy.

1. Introduction

Lycopene is a carotenoid pigment found in various fruits and vegetables, known for its antioxidant properties and potential health benefits (Tufail et al., 2024). It was found to possess the strongest antioxidant activity when examined among more than 600 types of naturally occurring carotenoids. Due to the high number of double bonds in its structure, lycopene exhibits significant antioxidant properties (Ozkan et al., 2023). The reactivity of free radicals with lycopene can vary between two- and tenfold, demonstrating its powerful antioxidant capability. In addition to being an effective antioxidant, lycopene also has antiteratogenic, anticarcinogenic, and cholesterol-lowering properties. For these reasons, lycopene is an important component that helps protect macromolecules from oxidative damage, improves the antioxidant balance in the human body, and regulates gene expression and immune responses (Ono et al., 2015).

As a consequence of increasing environmental concerns and limited economic opportunities, the valorisation and effective utilisation of fruit and vegetable waste have gained major significance (Afraz et al., 2023). The amount of waste generated as a result of food production constitutes 30% of all waste in the world, which means almost 1.3 billion tons of food waste (Castro et al., 2021). Tomatoes and tomato products are among the most abundantly consumed food products around the world. Tomato skins, which are often eliminated during the production of tomato concentrates and sauces, are a rich source of lycopene ($C_{40}H_{56}$) (Marinaccio et al., 2024). However, as a result of the applied processes, tomato peels, pulp and seeds emerge as industrial waste. It was found out that the lycopene content in skins is up to 5 times higher than in the pulp (Ozkan et al., 2023).

The variety of volatile compounds defines the flavour and aroma of a fruit or a vegetable (Göğüş et al., 2007; Zhang et al., 2023) and affects the decision of the consumers during purchase. The conducted literature has declared the identification of over 400 volatile compounds in tomato fruit (Klee, 2010). Furthermore, the amount and variety of volatiles were significantly influenced by internal (genetics) and external (pre and post-harvest) factors, including growth conditions, fertilisation, harvest maturity, and storage atmosphere, temperature, and duration (L. Wang et al., 2016).

Novel technologies have been introduced for the extraction of valuable compounds, and among these, subcritical and supercritical fluid extraction technology stands out due to its operational simplicity, low extraction temperature, and non-polluting characteristics (Baldino et al., 2017; Ozel, 2025). This novel approach helps to preserve the biological activity of the extracted compounds, increasing the extraction

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efficiency (Misra et al., 2017). Supercritical and subcritical extraction techniques stand for their environmentally friendly characteristics and benefits, such as providing solvent-free bio-extract, no post-extraction treatment, reduced extraction time, and high extraction yield, unless the utilised extraction fluid is considered as "safe" (Essien et al., 2020; Ozel, 2025).

Reducing reliance on toxic solvents, green and sustainable processes attract attention for the evaluation of agro-wastes to extract valuable bioactive compounds for their utilization as natural food ingredients, nutraceuticals, or pharmaceuticals (Özel, 2026). Implementing green analytical chemistry (GAC) principles within modern analytical methodologies, significant progress has been made by introducing miniaturised instruments, minimising solvent utilisation and easy-to-operate systems (Senila, 2026). Anastas and Warner defined the 12 principles of green chemistry in 1998 (Anastas and Eghbali, 2010), and it was then realised that these 12 concepts were not appropriate to analytical methods. These concepts were revisited by Gałuszka et al. to be compatible with analytical chemistry techniques (Gałuszka et al., 2013). Numerous assessment approaches were introduced to contribute to the evaluation of analytical methods. The Analytical Greenness (AGREE) calculator, relying on GAC's 12 criteria, was developed by Pena-Pereira et al. (Pena-Pereira et al., 2020a), and each criterion is translated into a scale of 0–1, yielding the overall analytical method's final assessment findings and displaying a coloured graph ranging from green-yellow-red representing the influence of each criterion. The methodology, with a score close to 1.0, displayed by an intense green pictogram, denotes that the suggested methodology is ecologically friendly.

Experimental design is a way to investigate the full effect of a particular variable, isolating the individual effect, assessing the interaction of variables with each other, and determining which variable can be neglected. Experimental design methods have been used for optimisation because they are faster, more economical and effective, and can optimise multiple variables simultaneously.

The objective of this study is to develop a sustainable process for the determination and recovery of valuable lycopene and volatile compounds (such as ketones, terpenes and aldehydes) from tomato waste products (peels, pomace and seeds) through ecologically friendly extraction methods by applying green chemistry principles, followed by evaluation of the physical and chemical features of these variable compounds. For the application of the green extraction procedure, subcritical ethanol extraction was utilised in a closed-vessel microwave reactor operating under controlled temperature and pressure conditions, where microwave energy was used solely to heat the extraction medium to the desired subcritical temperature. Enlightening the valuable composition of tomato products, this study demonstrates the potential of utilising tomato and /or tomato waste as a resource for natural additives in the food, cosmetic, and pharmaceutical industries, through valorisation. By promoting responsible management of tomato waste, reducing harmful environmental impacts, and minimising waste generation, the study will enhance the value of lycopene and volatile compounds, thereby establishing a sustainable value chain in these industries.

2. Materials and methods

2.1. Chemicals and instrumentation

Lycopene standard was purchased from VWR International Ltd. 2,2-Diphenyl−1-picrylhydrazyl (DPPH), HPLC grade methanol and acetonitrile (>99.9%) were supplied from Merck.

Mars 6 Microwave Accelerated Reaction System (CEM Corporation) was used for the extraction of lycopene from tomato samples, and antioxidant activity measurements were performed using a Shimadzu UV−2600 spectrophotometer. A Shimadzu Prominence-i LC-2030C Plus HPLC system coupled with diode array detector (DAD) was used for the analysis of lycopene. Volatile compounds were determined by an Agilent 8860 GC-MS System.

2.2. Sample preparation

Tomato samples were purchased from a local supermarket in Hatfield, UK. Tomato and tomato products were obtained from the same commercial product and the same lot to minimise the influence of biological variability. Tomato peel samples were obtained using a mechanical peeler, homogenised, and pooled before the extraction process to provide a representative sample. The samples were peeled off and separated into skin and paste. Skin and paste parts were ground by a food processor for homogenisation, followed by vacuum-filtering of the skin part. The paste, skin and juice were stored in amber bottles at 2–3 °C. Fig. 1 is displayed for a better understanding of the sample preparation procedure. As the Box-Behnken design generated by Design-Expert® Software Version 22.0.3 included 5 centre point experiments for the estimation of experimental error and adequacy, the extraction of the centre point conditions was replicated 5 times.

Subcritical extraction with 95% ethanol (*v/v*) solution was proposed for the extraction of the maximum amount of lycopene from tomato samples. The subcritical extraction method is considered a green method that does not require any additional energy source to enhance the extraction recovery. Before the use of 95% ethanol (*v/v*) solution, different compositions of water-ethanol solutions (water, 10% ethanol (*v/v*), 50% ethanol (*v/v*) were tested. Maximum extraction efficiency was obtained using 95% (*v/v*) ethanol solution, which may be explained by the lower subcritical temperature of ethanol when compared to water (Y. Wang et al., 2017). Subcritical water extraction is expected to have higher efficacy at increasing temperature values, which may lead to deterioration of lycopene and other bioactive components in tomato samples (Dai & Mumper, 2010). Thus, using 95% ethanol, operational parameters were adjusted as 30 min for extraction time, 140 °C for extraction temperature, and 3.0 g / 40 mL for sample/ solvent ratio. Microwave extraction system automatically applies power between 0 and 1000 W range and controls the temperature increase via a contactless *in-situ* temperature sensor that measures the sample temperature of each vessel in real time.

Commercial tomato paste, sauce and chopped tomato samples were purchased from a local market in UK. The proposed extraction method was also applied to the commercial samples in order to assess the lycopene content. Final extracts of commercial samples were filtered through 0.45 μm PTFE syringe filters and analysed. directly.

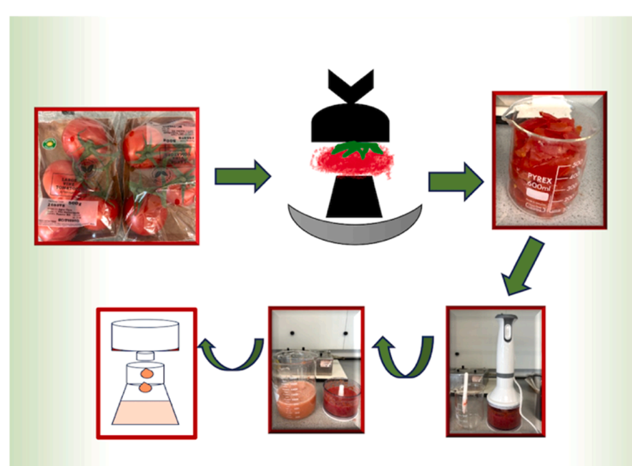

Fig. 1. Tomato sample preparation procedure.

2.3. Determination of lycopene

HPLC with DAD system coupled with Phenomenex C18 column (250 mm x 4.60 mm x 5 micron) was used for the analysis of lycopene. An isocratic elution program consisting of methanol: acetonitrile mobile phase (90:10) with a flow rate of 0.8 $mLmin^{-1}$ was installed for 40 min. Column temperature and injection volume were adjusted to 30 °C and 20 µL, respectively (Fagundes et al., 2015). Lycopene peak was identified at 470 nm. Calibration curves were constructed with the aid of linear equations of peak area *versus* lycopene concentration. A linear concentration range was studied with lycopene standards prepared in ethyl acetate at a 0–10 mgL^{-1} concentration range.

2.4. Volatile analysis

Volatile analysis of tomato peel and commercial tomato product extracts was performed with the aid of a GC-MS System. Helium was used as a carrier gas. The column was a non-polar BPX5 (30 m × 0.32 mm i.d. × 0.25 µm film thickness). The chemical composition of the extracts was analysed by Agilent gas chromatography (8850 GC) coupled to a mass spectrometry (5977 C GC MSD) for component identification. Hexadecane is a chemical substance which is added as an internal standard at the same concentration to all samples throughout a quantitative analysis. The initial oven temperature was 50 °C, held for 1 min, ramped at a rate of 8 °C min^{-1} to reach a final temperature of 250 °C and held for 1 min.

2.5. Free radical scavenging effect on DPPH

The assessment of free radical scavenging capacity is one of the most important antioxidant capacity parameters. The following protocol was applied for the determination of radical scavenging capacity of tomato peel extracts on DPPH: 3.0 mL 1×10^{-4} M methanolic DPPH solution was mixed with x mL of sample extract and (5-x) mL water in a test tube. The final mixture was allowed to stand in the dark for 30 min, followed by absorbance (A) measurement at 515 nm against the reagent blank. Absorbance change due to the reaction was evaluated as the antioxidant potential of the sample extracts and expressed in Equation 1.

$$\textit{Antioxidant Activity} \quad \% = \frac{A(control) - A(sample)}{A(control)} \times 100$$

2.6. Statistical analysis

Box-Behnken design was used to optimise the extraction parameters of lycopene. The responses and the factors are the two major types of variables of a multivariate optimisation procedure. The responses are the dependent variables that depend on the levels of the factors, which can be classified as qualitative or quantitative (Ferreira et al., 2007). Box-Behnken (Design-Expert® Software Version 22.0.3 (Stat-Ease, Inc., Minneapolis, USA)) was used to determine optimal conditions and investigate the effect of three variables (A: mass of sample (g), B: extraction temperature (∘C), C: extraction duration (min), on the following responses as lycopene amount (mg/g-WS) and antioxidant activity percentage (activity %). Table 1 summarises the factors and levels investigated within the study. Design-Expert program was used for the evaluation of the analysis of variance (ANOVA) test to examine the relationship between independent variables and responses.

3. Results and discussions

3.1. Experimental design and optimisation of subcritical ethanol extraction of lycopene from tomato peel

The impacts of sample amount, extraction temperature and extraction duration on lycopene efficiency and antioxidant activity % of tomato peels were evaluated using Box Behnken Design. The experimental results obtained as a result of the investigated parameters and experimental results are displayed in Table 1. Among 17 experiments conducted, the highest lycopene efficiency belongs to the 12 th run (5.0 g sample, 140 ^{0}C, 30 min), whereas the highest antioxidant activity was provided by the 15th run. This absence of correlation between lycopene amount and antioxidant activity in tomato peel extracts may be explained by the structural variations in the antioxidant molecules and interactions among the phytochemicals (Slimani et al., 2025). The coded quadratic lycopene efficiency and antioxidant activity (%) models for tomato peel samples are specified by Eq. (2) and (3). Additionally, the significance of each coefficient was determined using the F test and p-value (Tables 2, 3), where the importance of the corresponding variables was indicated by high F-values and low p-values.

$$\textit{Lycopene amount} \quad (mg\ lycopene/\ g^{-1} WS) \quad = \quad +2.940 + \quad 1.220A + \quad 0.4725B - \quad 0.1288C + \quad 0.9825AB + \quad 0.7475BC + \quad 1.930C^2 \tag{2}$$

$$\textit{Antioxidant Activity}\,(\%) = \; +78.67 + \; 12.14A - \; 0.08700B - \; 0.6500C - \; 6.20A^2 \tag{3}$$

Achieving high lycopene efficacy from tomato peels was the main target of this study. The reduced quadratic model of lycopene efficiency

Table 1
Independent factors and experimental results of Box-Behnken design of subcritical ethanol extraction of lycopene.

Run Number	The Independent Factors				
	Mass of sample (g)	Extraction temperature (∘C)	Extraction duration (min)	Lycopene amount (mg g^{-1}WS)	Antioxidant activity %
1	3	140	20	2.89	74.0
2	1	140	10	2.76	79.7
3	3	110	30	5.74	75.0
4	3	110	10	5.61	76.8
5	5	110	20	2.46	60.0
6	1	110	20	2.88	85.3
7	3	140	20	2.97	80.0
8	1	170	20	3.49	75.7
9	3	140	20	3.25	63.0
10	3	170	30	3.35	65.0
11	5	170	20	1.76	53.3
12	5	140	30	6.51	81.8
13	1	140	30	6.13	80.0
14	5	140	10	2.80	75.0
15	3	170	10	2.37	91.6
16	3	140	20	4.87	86.5
17	3	140	20	5.60	85.0

Table 2
ANOVA results of the quadratic equations from Box-Behnken for the lycopene extraction efficiency response in tomato peel using subcritical 90% ethanol solution extraction.

	Sum of squares	df	Mean Square	F-value	p-value
Model	35.70	6	5.95	39.46	< 0.0001
A	11.98	1	11.98	79.46	< 0.0001
B	1.79	1	1.79	11.85	0.0063
C	0.13	1	0.13	0.88	0.3704
AB	3.86	1	3.86	25.61	0.0005
AC	2.24	1	2.24	14.82	0.0032
BC	15.70	1	15.70	104.14	< 0.0001
A^2	1.51	1	5.95	39.46	< 0.0001
B^2	1.48	1	11.98	79.46	< 0.0001
C^2	0.03	1	1.79	11.85	0.0063
Residual	1.51	10		0.15	
Lack of Fit	1.48	6	0.01	0.25	36.5600
Pure Error	0.03	4		0.01	
Corrected Total	37.20	16			

Table 3
ANOVA results of the quadratic equations from Box-Behnken for the AOX activity response in tomato peel using subcritical 95% ethanol solution extraction.

	Sum of squares	df	Mean Square	F-value	p-value
Model	1345.02	4	336.25	12.52	0.0003
A	1178.55	1	1178.55	43.87	< 0.0001
B	0.06	1	0.06	0.01	0.9627
C	3.38	1	3.38	0.13	0.7290
A^2	163.02	1	163.02	6.07	0.0298
Residual	322.35	12	26.86		
Lack of Fit	240.37	8	30.05	1.47	0.3763
Pure Error	81.98	4	20.50		
Corrected Total	1667.36	16			

was found to be statistically significant ($F = 39.46$, $p < 0.001$) with a high coefficient of determination ($R^2 = 0.9595$), proposing that the selected factors explain the variation in the response values. The adjusted R^2 value (0.9352) further confirms the adequacy of the selected model terms, while the predicted R^2 value (0.8023) is in reasonable agreement with the adjusted R^2, demonstrating good predictive capability and limited overfitting. The relatively low coefficient of variation (C.V. = 10.09%) suggests satisfactory experimental precision and reliability of the obtained data. In addition, the adequate precision value of 20.11, which is well above the recommended threshold of 4, indicates a strong signal-to-noise ratio, confirming that the model can be effectively used to navigate the design space. Among the studied variables, the mass of waste (A) and temperature (B) exerted significant effects ($p < 0.05$) on lycopene yield, while the extraction duration (C) had a statistically non-significant contribution. Lycopene recovery is majorly influenced by the interaction terms AB and BC ($p < 0.01$) reveals that the combined effects of mass–temperature and temperature–duration play a significant role in the model. Moreover, the highly significant quadratic term of duration C^2 ($p < 0.001$) indicates a pronounced curvature effect, suggesting the presence of an optimum extraction duration rather than a simple linear relationship. Importantly, the strong agreement between predicted and adjusted R^2 values, together with the high adequacy precision, suggests that the model successfully captures the dominant trends governing lycopene extraction and is suitable for interpreting factor effects and optimisation purposes, with confirmation experiments recommended to further validate model predictions.

The analysis of variance (ANOVA) for the reduced quadratic model describing antioxidant activity demonstrates that the model is statistically significant ($F = 12.52$, $p < 0.001$), indicating that the selected factors sufficiently explain the variations in the response. Among the investigated terms, the mass of waste (A) exhibited a highly significant linear effect ($p < 0.001$), highlighting its dominant influence on antioxidant activity, while the quadratic term A^2 was also significant ($p < 0.05$), suggesting a curvature effect. In contrast, temperature (B) and extraction duration (C) did not show statistically significant linear effects within the studied range ($p > 0.05$). Correlation coefficient value ($R^2 = 0.807$) and adjusted value ($R^2 = 0.742$) support the reliability of the model, confirming satisfactory explanatory power. Moreover, the predicted R^2 value (0.574) shows reasonable agreement with the adjusted R^2, suggesting acceptable predictive performance. The relatively low coefficient of variation (C.V. = 6.84%) reflects good experimental precision, while an adequate precision value of 9.10, being above the recommended threshold, confirms a sufficient signal-to-noise ratio. Overall, the reduced quadratic model is suitable for interpreting the effects of key variables and for navigating the design space to optimise antioxidant activity.

3.2. Effect of operational parameters

Operational parameters that have a significant influence on lycopene extraction and AOX activity of tomato peels, such as extraction duration, temperature, and mass of tomato peel were investigated. The effects of operational parameters on lycopene extraction were displayed in Fig. 2, with the aid of two-dimensional (2-D) contour plots and three-dimensional (3-D) graphs.

In this context, the optimal conditions presented by the model were evaluated from many aspects (workload, solvent consumption, environmental concerns, etc.), and the most suitable conditions were evaluated. Fig. 2a illustrates the combined effect of mass of tomato peel (g) and temperature (°C) on the lycopene yield (mg/g) while keeping the duration factor constant at 20 min. The colour gradient (from blue to yellow) represents increasing lycopene concentration, ranging approximately from 1.76 to 6.51 $mg.g^{-1}$. At decreasing temperature values (110–130 °C), the response remains minimal regardless of the amount of tomato peel, whereas at increasing temperature values (160–170 °C), a dramatic increase in lycopene recovery is observed, displaying a strong correlation between lycopene yield and temperature. This behaviour points to improved cell matrix breakdown and mass transfer at higher temperatures, which would promote lycopene release, which was previously highlighted in earlier studies (Kehili et al., 2019,MacHmudah et al., 2012).

The effect of the tomato peel amount is displayed in Fig. 2b. It should be pointed out that the mass of tomato peel increased, whereas the volume of the extracting solution remained constant at 40 mL, through the optimisation procedure. At a constant temperature value, increasing amounts of tomato peel (1.0–5.0 g) lead to higher lycopene efficiency, although the effect is less dominant compared to the temperature factor. This indicates that the substrate availability, having a moderate influence on extraction efficiency, is not a controlling factor in the model. Similar results were reported by Gu et al., who stated that no significant increase in lycopene yield was observed when the solvent: solid ratio was increased from 40 to 130 mL/mg (Gu et al., 2008). Temperature and mass of tomato peel interact significantly, as shown by the curved contour lines and slanted surface, intensifying the positive impact of increasing amounts of waste at higher temperatures.

The three-dimensional response surface illustrates the combined effects of mass of tomato peel (g) and temperature (°C) on antioxidant activity (%), at adjusted extraction duration of 20 min. The colour gradient indicates antioxidant activity values ranging from approximately 53.3% to 91.6%, with higher values represented by yellow regions. Temperature displays a nonlinear effect on antioxidant activity. Increasing the temperature to moderate values enhances the AOX activity by reducing the viscosity of the solvent and enabling the release of bioactive compounds into the extraction medium. Beyond this region, a slight decline is observed, which may be explained by thermal degradation of antioxidant compounds at excessive temperatures (Elmas et al., 2025).

The mass of tomato peel shows a significant quadratic effect on antioxidant activity. Antioxidant activity increases with increasing peel mass up to an optimal level (approximately 5–7 g), after which further increases result in a decrease. This behaviour suggests that excessive solid loading may hinder mass transfer, reduce effective solvent–solid contact, or promote incomplete extraction due to the limited solvent availability.

3.3. Lycopene efficacy of extracted tomato peel samples and commercial products

The screening of lycopene content in tomato peel and commercial tomato product extracts was carried out using an HPLC–DAD system. The retention times, working ranges, calibration equations, and correlation coefficients for lycopene identified in the extracts are summarised in Table 4.

In addition, a chromatogram of 5.0 mgL^{-1} lycopene and tomato peel extract (1.0 g, 140°C, 20 min) at 470 nm is shown in Fig. 4.

Lycopene amounts of tomato peel extracts and commercial products were evaluated under optimum conditions (3.0 g sample, 140°C, 20 min), followed by chromatographic analysis. Under the examined

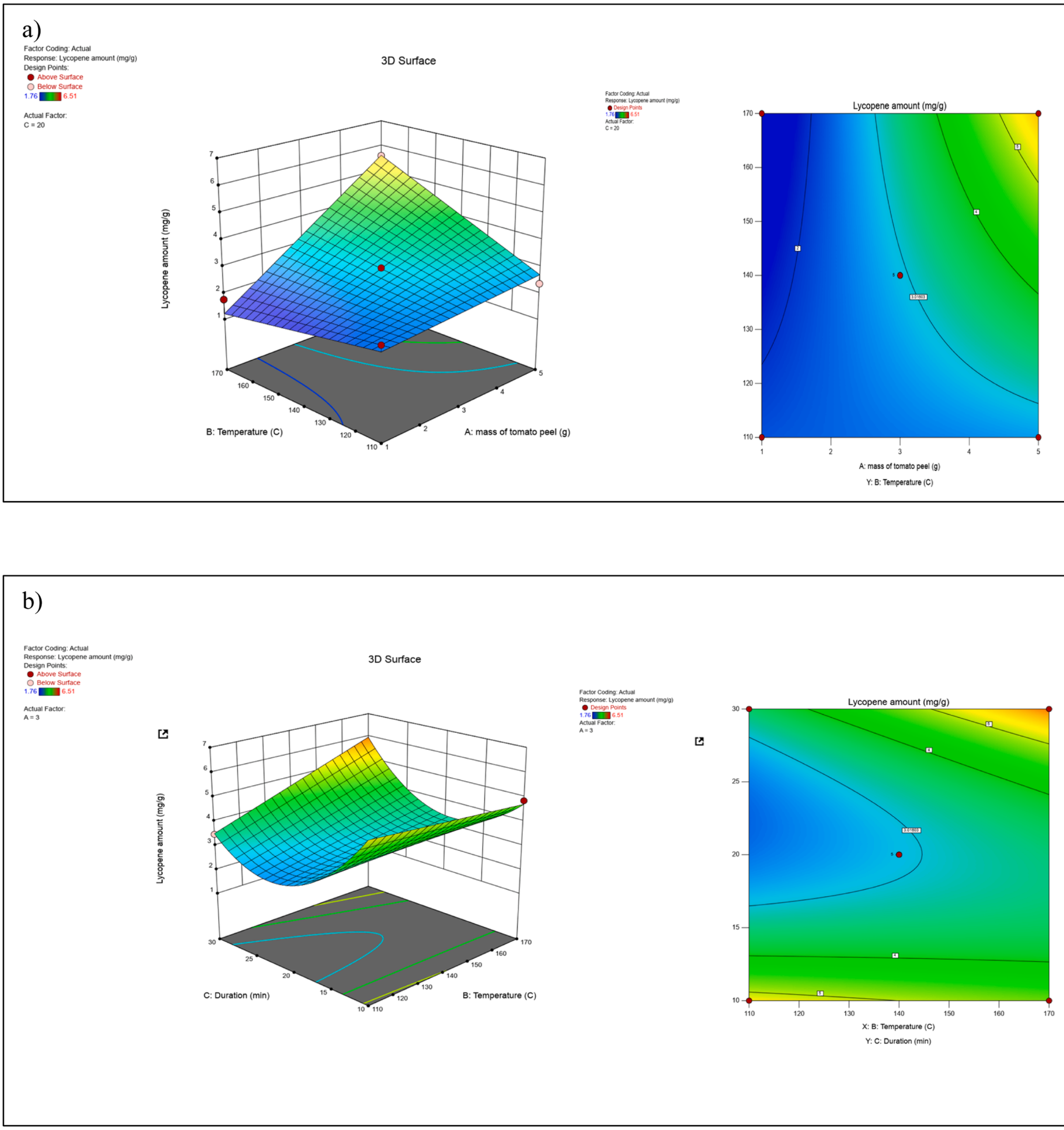

Fig. 2. 2-D contour plot and 3-D graph for the lycopene (mgg^{-1} WS) of the tomato peel extract as a function of a) Mass of tomato peel (g) and temperature (°C), b) Temperature (°C) and extraction duration (min).

experimental conditions, the mean lycopene concentration of the tomato peel sample was 2.94 mg g^{-1} WS, suggesting a moderate extraction yield. Good experimental repeatability is indicated by the comparatively low coefficient of variation (3%) and standard deviation (0.39 mg/g), which implies a slight dispersion around the mean. The range of lycopene levels from 1.12 to 4.77 mg/g showed that the process variables had a regulated and detectable impact on the recovery of lycopene. Various extraction techniques were suggested to recover lycopene from tomato, such as microwave-assisted extraction (MAE), ultrasound-assisted extraction, methods involving different extraction aiders as enzymes, supercritical fluid or vegetable oils (Méndez-Carmona et al., 2022).

In order to estimate the daily intake levels of lycopene, commonly consumed tomato products were purchased from a local supermarket and analysed for their lycopene contents and predetermined optimum conditions of the extraction model (3.0 g, 140°C, 20 min) were applied. Table 6 summarises the lycopene amount in mg g^{-1} WS determined by HPLC.

Among the revealed results, the highest lycopene content belongs to TS7 followed by TS1. In a study on the evaluation of lycopene in commercial products conducted in 1998, paste, puree and canned tomatoes had the highest lycopene levels, ranging from 195 to 365 ppm, whereas

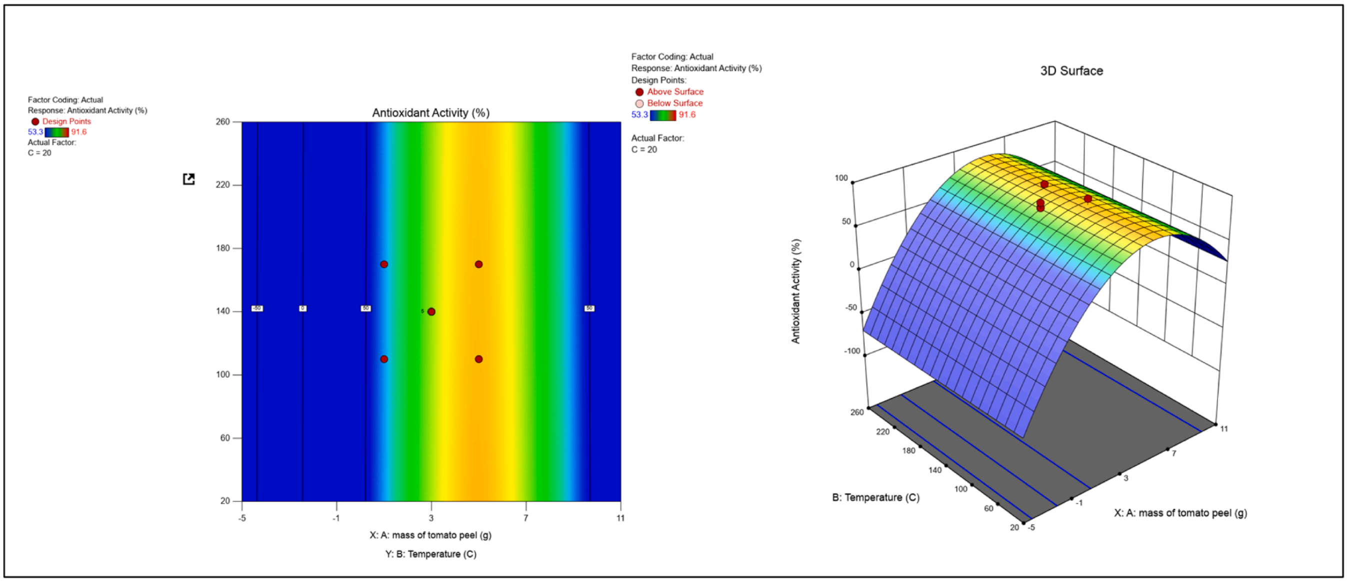

Fig. 3. 2-D contour plot and 3-D graph for the AOX activity (%) of the tomato peel extract as a function of temperature (°C) and mass of tomato peel (g).

Table 4
Retention time, working range, linear calibration equation and correlation coefficient of lycopene.

Compound	Retention time (t_R)	Working Range (mgL^{-1})	Calibration Equation	Correlation Coefficient (R^2)	LOD (mgL^{-1})	LOQ (mgL^{-1})
Lycopene	29.70	0.5–10.0	$y = 13262\ C_{lycopene}$	0.9967	0.17	0.59

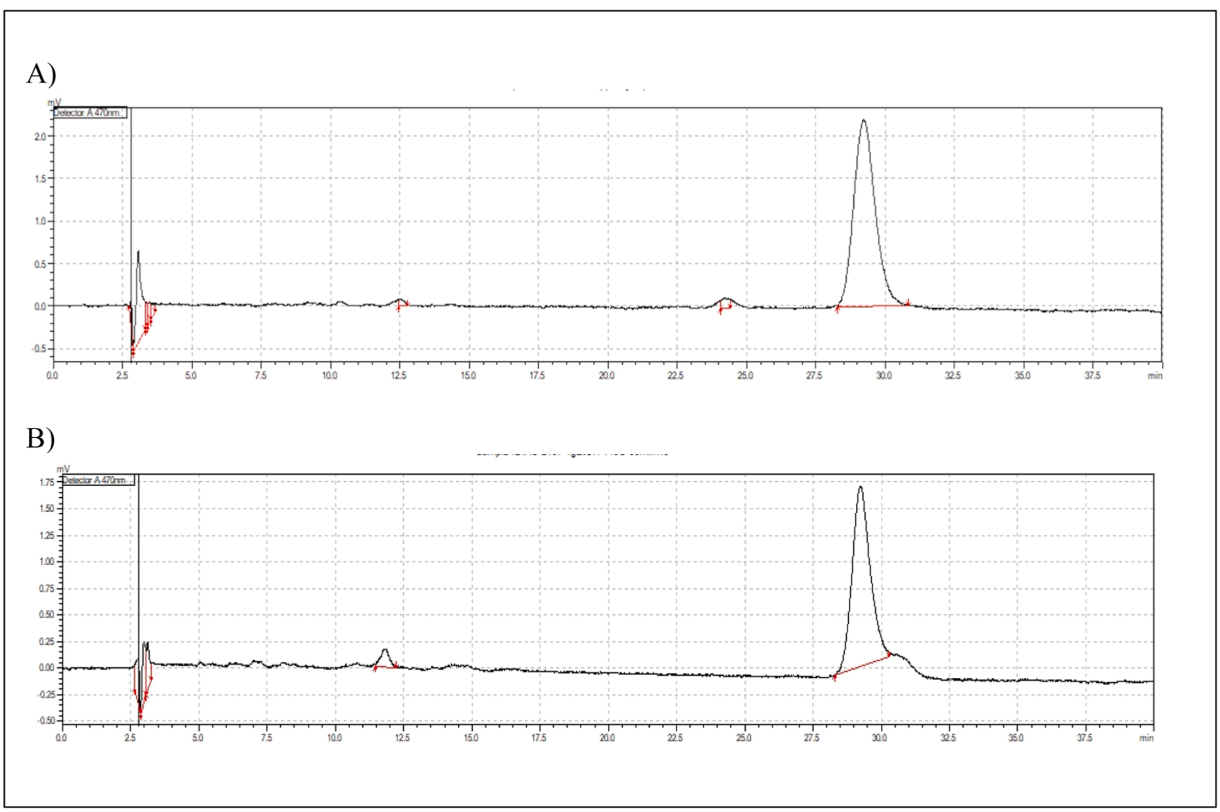

Fig. 4. HPLC Chromatogram of A) 5.0 mgL^{-1} lycopene standard solution (top figure), and B) Tomato peel extract (1.0 g, 140°C, 20 min) at 470 nm (bottom figure).

Table 5
Comparison of lycopene extraction methods.

Method	Lycopene Amount	Operational Parameters	Reference
Enzyme-assisted extraction using rice-bran oil	3.99 mg g^{-1} DW tomato peel	52°C, 92 min, 100 mL extraction solvent	(Tran and Nguyen, 2023)
Supercritical carbon dioxide	0.320 mg kg^{-1}raw material tomato process by-product	80°C, 50 MPa	(Hatami et al., 2019)
MAE solvent	0.14 mg g^{-1}	Ethyl acetate, 1 min, 400 W	(Ho et al., 2015)
Acetone and n-hexane extraction from tomato waste	3.47–4.03 mg 100 g waste	1:3, 2:3, 3:1 (*v/v*) 30, 40, 50 °C	(Poojary and Passamonti, 2015)
Cell-wall degrading enzymes	4.40 mg g^{-1} DW tomato peel	1-h enzyme incubation followed by a 3-h solvent (Hexane, ethyl acetate and the mixture hexane/ acetone/ethanol 50:25:25 (*v/v*) extraction at 40 C	(Lavecchia and Zuorro, 2008)
Hexane: acetone: ethanol (2:1:1, *v/v/v*)	6.22 ± 0.63 µg g^{-1} DW	Room temperature for 10 min to facilitate pigment solubilization.	(Becze et al., 2025)
Subcritical ethanol extraction	6.51 mg g^{-1} WS	5.0 g sample, 140°C, 30 min	This study

Table 6
Lycopene content in tomato products.

Commercial Tomato Samples	Lycopene Amount on WS(mg g^{-1})
TS1 (ketchup)	2.066
TS2 (chopped tomato)	1.109
TS3 (chopped tomato)	1.051
TS4 (crushed tomato)	1.422
TS5 (tomato pasta sauce)	0.244
TS6 (tomato pasta sauce)	0.827
TS7 (tomato puree)	3.852
TS8 (chopped tomato)	1.135
TS9 (chopped tomato)	0.653
TS10 (smooth tomato)	0.903
TS11 (tomato chilli sauce)	0.937
TS12 (tomato paste)	0.123

ketchup and sauces had from low to moderate lycopene levels (43–140 ppm) (Rao et al., 1998). In the present study, the lycopene contents of ketchup and tomato sauces were observed to be close to the highest reported levels. These findings may support the potential incorporation of externally added lycopene as a food additive to optimise and standardise the functional properties of these products.

3.4. Volatile analysis

Volatile analysis of tomato peel samples after subcritical 95% ethanol (*v/v*) extraction was performed. Quantitative data of each run are given in Table 7 using the internal standard (hexadecane) method. Table 8 is identified in tomato peel, with their retention times and relative abundances (Run number 6) of main compounds. The yields are given as weight per cent on the basis of 100 g of tomato peel. The main components of the volatiles of tomato peel are 1-acetate, 1,2,3-propanetriol and 2,3-dihydro−3,5-dihydroxy−6-methyl-4H-pyran−4-one. They are mainly oxygenated compounds. Benzeneacetaldehyde is a good flavour molecule.

Table 7
Quantitative GC-MS data on 17 extracts.

Run Number	Total Amount Volatile Content
1	0.18
2	0.19
3	0.16
4	0.14
5	0.07
6	0.44
7	0.20
8	0.11
9	0.25
10	0.69
11	0.19
12	0.11
13	0.10
14	0.20
15	0.22
16	0.10
17	0.06

Table 8
Volatile compounds, retention times, and percentage compositions of tomato peel compounds for run number 6 of subcritical ethanol extraction.

Compound[a]	RI[b]	t_R (min)	%[c]
1-Fluoro−2-propanone,	676	3.45	0.021
Methyl pyrazine,	805	3.66	0.015
2-Furanmethanol	862	4.13	0.013
Dihydroxyacetone	893	4.73	0.037
3-Methyl−2,5-furandion	949	5.61	0.023
4-Hydroxy−5-methyl−3(2 H)-furanone	1040	7.27	0.021
Benzeneacetaldehyde	1050	7.47	0.014
2,4-Dihydro−2,4,5-trimethyl-3H-pyrazol−3-one	1060	7.98	0.012
2,3-Dihydro−3,5-dihydroxy−6-methyl-4H-pyran−4-one	1167	9.31	0.059
1-Acetate 1,2,3-propanetriol	1260	11.03	0.060
4-Ethyl hydrogen itaconate	1310	11.11	0.024
DL-Proline, 5-oxo-, ethyl ester	1447	14.37	0.027
TOTAL			0.326

[a] As identified by GC-MS software; names according to NIST mass spectral library, and by comparing their Kovats retention indices.
[b] Kovats retention indices
[c] The percentage of each component is calculated as the concentration in the tomato peel sample

Over 400 volatile aromatic compounds determine and constitute the majority of flavour of tomatoes (Klee, 2010). Many volatile compounds such as aldehydes, alcohols, ketones, esters, phenols and sulfurs have a significant influence on tomato flavour (Li et al., 2020). This study identified 51 volatile compounds.

3.5. Antioxidant activity of extracted samples

Antioxidant activity and total antioxidant capacity of tomato fruit vary with either the fragments of the fruit or the tomato varieties. Earlier studies have shown that the antioxidant activity of tomato is directly related to the individual compounds, such as ferulic acid, caffeic acid and lycopene (Guil-Guerrero & Rebolloso-Fuentes, 2009; Poojary & Passamonti, 2015). Therefore, the antioxidant (AOX) activities (%) of the tomato peel extracts were quantitatively determined and are displayed in Table 1. The AOX values ranged from 53.3 to 91.6%, demonstrating a significant antioxidant capacity of the peel extracts. This substantial variability may be attributed to the compositional heterogeneity of the peel matrix and the differences in the extraction conditions. The present findings are in strong agreement with previous reports by Grassino and Conti (Conti et al., 2022; Ninčević Grassino et al., 2020), which consistently indicates that tomato peel is significantly richer in bioactive constituents than the pulp. These results further highlight the valorisation potential of tomato peel as a functional ingredient and a promising source of natural antioxidants.

3.6. Greenness evaluation of lycopene extraction

Evaluation of the environmental performance of extraction processes used for the recovery of lycopene from tomato products is significant before labelling the proposed method as "green". The greenness of this study was discussed using AGREE (Pena-Pereira et al., 2020b), an analytical metric for environmental performance assessment. To fully evaluate the greenness of an analytical method, the criteria should address the type and amount of materials used, the waste produced, the energy required, the analyst's safety, and overall methodological aspects such as the number of pretreatment steps and how close the analytical instrument is to the sample being examined. The AGREE result illustrating the analytical greenness performance of the subcritical extraction method is presented in Fig. 5. The score revealed that the subcritical lycopene extraction, with a final score of 0.7, may be suggested as an environmentally friendly process. The procedure involves external sample treatment with a reduced number of steps (principle 1), and 3.0 g of tomato sample was required (p 2). The measurement is off-line (p 3), and the procedure involves minimized number of steps (p 4). The procedure is semi-automated (p 5). No derivatisation agents are involved in the extraction process (p 6). Analytical wastes include the sample itself (3.0 g), 40 mL of 95% ethanol solution (*v/v*), (p 7). Twelve analytes are determined in a single run, and the sample throughput is 36 h^{-1}, based on the subcritical extraction time of 20 min (p 8). As MAE is one of the most sustainable applications, adhering to green chemistry principles may be considered as an option for lycopene recovery from tomato products (p 9), and some of the reagents (alcohols) can be from bio-based sources (p 10). The procedure does not require toxic solvents (p 11), and EtOH is considered highly flammable (p 12).

Conventional lycopene extraction is based on the installation of organic solvents such as acetone, petroleum ether, chloroform, hexane, etc (Psillakis & Pena-Pereira, 2024). The use of subcritical ethanol extraction for the recovery of lycopene alters the physical and chemical properties of EtOH solution, transforming it into a highly efficient extraction medium for compounds such as essential oils, phenolics, organic acids, carotenoids, and other bioactive molecules and eliminates the need for toxic organic solvents, leading a more environmentally friendly extraction technique.

AGREE evaluation of the current study also supports the need for continuous improvement in extraction methodologies, by integrating more applications of alternative solvents and reducing the environmental impact of analytical chemistry and transitioning to a circular economy (Psillakis & Pena-Pereira, 2024).

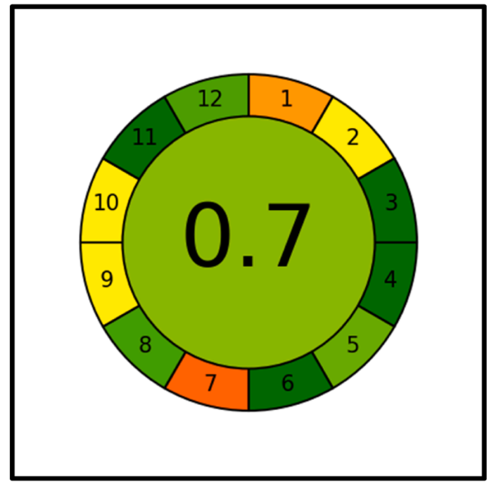

Fig. 5. AGREE illustration of subcritical extraction of lycopene.

4. Conclusions

This study successfully optimised the extraction of lycopene from tomato peels using subcritical ethanol, identifying key operational parameters such as extraction temperature and sample mass that significantly influence both lycopene yield and antioxidant activity. The Box-Behnken Design method provided a robust framework for evaluating these factors, demonstrating high predictive accuracy and model significance. The findings indicate that optimal extraction conditions lead to a moderate recovery of lycopene, underlining the potential of tomato peels as a valuable source of bioactive compounds. Moreover, the evaluation of the environmentally friendly nature of the extraction technique highlights its compliance with green chemistry principles, advocating for its adoption in future processes.

This work demonstrates the efficacy of subcritical ethanol green extraction for the recovery of lycopene from tomato peel and commercial tomato products. As far as we are aware, this is the first study investigating the subcritical ethanol extraction of lycopene from tomato peel. The findings underscore the significance of optimising operational parameters for maximum yield of extraction while maintaining the integrity of bioactive compounds. Under optimal conditions, the highest lycopene values for tomato peel extracts were found as 6.51 mg g^{-1} compared to the literature. AGREE metric tool software was used to evaluate the greenness of the lycopene extraction process to evaluate the method from an environmental point of view. The results revealed that the subcritical extraction process was scored as 0.7. The present findings, impacting the valuable composition of tomato products/wastes, contribute to the sustainable valorisation of tomato products/wastes by establishing an environmentally friendly extraction approach with direct relevance to food applications. Overall, the results emphasise the importance of valorising tomato peel waste, not only for enhancing the nutritional profiles of products but also for promoting sustainability in extraction methodologies.

CRediT authorship contribution statement

Fatos Ayca Ozdemir Olgun: Conceptualisation, Investigation, Methodology, Experimental study, Software, Visualisation, Validation, Writing, Original draft preparation. **Mustafa Zafer Özel:** Supervision, Conceptualisation, Investigation, Methodology, Experimental study, Visualisation, Validation, Writing, Reviewing and Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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