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Extraction of lycopene from tomato processing waste: Kinetics and modelling

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ABSTRACT

Lycopene, a nutraceutical compound, was extracted from tomato processing waste, an abundantly available food industry by-product in Italy. The extraction kinetics was mathematically described using the first order kinetic model, the mass transfer model and Peleg's model to understand the physicochemical behaviour of the extraction. Samples were extracted using acetone/n-hexane mixtures at different ratios (1:3, 2:2 and 3:1, v/v) and at different temperatures (30, 40 and 50 °C) and simultaneously analysed using UV–VIS spectrophotometry. The lycopene yield was in the range 3.47–4.03 mg/100 g, which corresponds to a percentage recovery of 65.22–75.75. All kinetic models gave a good fit to the experimental data, but the best one was Peleg's model, having the highest R^2_{Adj} and the lowest RMSE, MBE and χ^2 values. All the models confirmed that a temperature of 30 °C and solvent mixture of acetone/n-hexane 1:3 (v/v) provided optimal conditions for extraction of lycopene.

1. Introduction

Lycopene, a bright red pigment, belongs to the carotenoid family and has received great interest due to its various biological activities. Lycopene acts as a potent antioxidant and contributes towards reducing the risk of chronic diseases by protecting cells against oxidative damage (Rao & Agarwal, 1999). Epidemiological and case-control studies as well as research on cell cultures and animals have shown that increased dietary consumption of tomatoes and tomato products containing lycopene is associated with decreased risk of prostate and breast cancer (Chalabi et al., 2006; Holzapfel et al., 2013). Studies have also revealed its protective effect on cardiovascular (Arab & Steck, 2000) and coronary heart diseases (Clinton, 1998). It inhibits low-density lipoprotein oxidation and helps to reduce cholesterol levels in the blood (Rao & Agarwal, 1999). Lycopene exhibits anti-inflammatory activity by inhibiting the activation of inducible nitric oxide synthase proteins (Rafi, Yadav, & Reyes, 2007). In the food industry, lycopene from tomato products is used as a food additive to enhance storage stability, nutritional properties and health benefits (Østerlie & Lerfall, 2005).

Though lycopene is found in watermelon, pink grapefruit, guava, and rosehip, the richest source is tomato. Not only can it be extracted from fresh tomato, but adequate quantities can also be obtained from tomato processing waste or tomato pomace (Zuorro, Fidaleo, & Lavecchia, 2011). The wet pomace contains about 33% seed, 27% skin and 40% pulp, whilst the dried form contains about 44% seed and 56% skin and pulp (Perretti et al., 2013). The lycopene content present in the skin fraction of tomato pomace is about 5 times higher than in the pulp (Papaioannou & Karabelas, 2012).

Italy produces about 38% of the tomatoes grown in the European Union, over 4 million tons annually, roughly 90% of which is intended for processing (Global Agricultural Information Network). According to the World Processing Tomato Council (WPTC), Italy produces about 200,000 t of tomato processing waste annually, whilst the worldwide production is more than 1,200,000 t (Zuorro et al., 2011). At present, the tomato processing waste is either discarded or used as animal fodder, but its abundance in lycopene makes it a promising prospect as a sustainable, alternative and low-cost source of this nutraceutical compound.

Lycopene is more commonly extracted with organic solvents such as hexane, acetone, ethanol, chloroform, petroleum ether, etc. (Berg et al., 2000; Naviglio, Caruso, Iannece, Aragòn, & Santini, 2008; Sadler, Davis, & Dezman, 1990; Xu & Pan, 2013). Since lycopene extracted using hexane/acetone or hexane/ethanol is more stable than that extracted using methanol or dichloromethane (Taungbodhitham, Jones, Wahlqvist, & Briggs, 1998), a solvent mixture consisting of hexane/acetone, hexane/acetone/

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ethanol is often used (Lin & Chen, 2003; Taungbodhitham et al., 1998). Recently, several advanced methods to extract lycopene from tomato have also been described, amongst them supercritical fluid extraction (Zuknik, Nik Norulaini, & Mohd Omar, 2012), ultrasound assisted extraction (Eh & Teoh, 2012), ultrasound-microwave extraction (Lianfu & Zelong, 2008), and enzyme assisted extraction (Zuorro et al., 2011) etc.

The kinetic description of solid–liquid extraction helps to design, optimise and simulate the extraction processes and to manage time and energy. In this study, we have modelled lycopene extraction from tomato processing waste, and examined the effects of two independent variables, namely temperature and solvent composition, on the kinetics of extraction.

2. Materials and methods

2.1. Materials

Tomato processing waste devoid of seeds was obtained from Pezziol SPA, Parma, Italy. The average particle size and water content of the sample were $\leqslant$0.5 mm and 35%, respectively. HPLC grade acetone, n-hexane, methanol and acetonitrile were purchased from Sigma–Aldrich, USA. Lycopene standard of HPLC grade ($\geqslant$95%) and solid sodium chloride (NaCl) ($\geqslant$99.5%) were obtained from Sigma–Aldrich, USA. Milli-Q ultrapure water with a resistivity of 18.3 MΩ cm was used in all the steps (Millipore, Germany).

2.2. Lycopene extraction and analysis

Lycopene extraction was carried out in a 35 ml screw-top vial placed in a thermostated water bath (±0.1 °C). 0.5 g of sample was added to the vial and agitated with 20 ml of acetone/n-hexane mixture under appropriate conditions (Tables 1–3). The vial was connected to a peristaltic pump that continuously draws the extract and passes it through a quartz flow cell (Hellma, Germany), mounted on a UV–VIS spectrophotometer (HP 8452A Diode Array Spectrophotometer, Agilent, USA). The extract was passed through a 0.45 μm hydrophobic PTFE membrane filter (Whatman) to eliminate suspended solids before entering the quartz flow cell. Absorbance of the extract was measured continuously every 60 s for 45 min at 472 and 503 nm against a blank of pure solvent mixture. To minimise the interference from other carotenoids, the concentration of lycopene was calculated at 503 nm using the molar extinction coefficient $17.2 \times 10^4\ M^{-1}\ cm^{-1}$ (Fish, Perkins-Veazie, & Collins, 2002). Lycopene content was expressed as mg/100 g fresh weight.

In a second set of experiments, we sought to determine how washing the extract with an aqueous NaCl solution affected the results. At set times (5, 10, 15, 20 and 40 min), 1.00 ml of extract was pipetted manually and washed with 10.0 ml of 1 M NaCl solution for 15 min and allowed for phase separation. Absorbance of the hexane layer (dehydrated with the addition of anhydrous $CaCO_3$) was measured against a hexane blank and compared with absorbance of non washed extract.

2.3. Total lycopene content determination

Total lycopene content was determined according to Fish et al. (2002) with minor modifications. Briefly, 1.0 g of sample was extracted with 30 ml of acetone/n-hexane (1:3, v/v) for 15 min and the extraction procedure was repeated until absorbance of the extract at 503 nm was lower than the instrumental noise

Table 1
Calculated parameters of the first order kinetic model at different extraction conditions.

Extraction conditions		C_{eq} (mg/100 g) (SE)	k (min^{-1}) (SE)	R^2_{Adj}	RMSE	MBE	χ^2
Solvent ratio acetone/n-hexane (v/v)	Temperature (°C)						
1:3	30	3.902 (0.021)	0.840 (0.057)	0.952	0.13718	0.01882	0.01882
	40	3.785 (0.029)	0.362 (0.022)	0.938	0.17505	0.03064	0.03064
	50	3.6841 (0.041)	0.269 (0.019)	0.894	0.23230	0.05396	0.05396
2:2	30	3.755 (0.027)	0.200 (0.008)	0.968	0.14463	0.02092	0.02092
	40	3.562 (0.043)	0.136 (0.007)	0.947	0.18739	0.03512	0.03512
	50	3.540 (0.036)	0.525 (0.050)	0.868	0.22154	0.04908	0.04098
3:1	30	3.552 (0.004)	2.738 (0.129)	0.997	0.02953	0.00087	0.00081
	40	3.355 (0.029)	0.542 (0.0457)	0.899	0.18205	0.03314	0.02853
	50	3.353 (0.036)	0.152 (0.0077)	0.950	0.16890	0.02853	0.00619
Average				0.935	0.16428	0.03012	0.02621

Table 2
Calculated parameters of the mass transfer model at different extraction conditions.

Extraction conditions		K_{obs} (min^{-1}) (SE)*	C_{eq} (mg/100 g) (SE)	a	R^2_{Adj}	RMSE	MBE	χ^2
Solvent ratio acetone/n-hexane (v/v)	Temperature (°C)							
1:3	30	0.803 (0.060)	3.904 (0.021)	0.037 (0.035)	0.951	0.13709	0.01879	0.01879
	40	0.296 (0.021)	3.807 (0.028)	0.138 (0.040)	0.949	0.15862	0.02516	0.02516
	50	0.183 (0.015)	3.747 (0.037)	0.245 (0.046)	0.932	0.18591	0.03456	0.03456
2:2	30	0.168 (0.007)	3.790 (0.025)	0.123 (0.025)	0.979	0.11845	0.01403	0.01403
	40	0.100 (0.005)	3.669 (0.039)	0.187 (0.024)	0.976	0.12504	0.01564	0.01564
	50	0.378 (0.042)	3.568 (0.035)	0.177 (0.061)	0.881	0.20968	0.04397	0.04396
3:1	30	3.891 (0.000)	3.547 (0.006)	0.001 (0.010)	0.993	0.04516	0.00204	0.00204
	40	0.433 (0.042)	3.371 (0.013)	0.136 (0.054)	0.908	0.17368	0.03016	0.03017
	50	0.115 (0.006)	3.430 (0.032)	0.180 (0.025)	0.976	0.11784	0.01389	0.01389
Average					0.949	0.14127	0.02203	0.02202

* Values of 0.000 indicate a standard error less than 0.001.