

# EXTRACTION KINETICS OF NATURAL ANTIOXIDANTS FROM POTATO BY-PRODUCTS

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Potato by-products contain phenolic compounds with antioxidant properties considered relevant to prevent some human diseases. These natural antioxidants can be also extracted and used in food industry to prevent the decay by peroxidation of lipid bearing foods. The recovery of these compounds requires however the use of mild extraction technologies, in order to preserve the antioxidant power. In such a contest, the extraction with supercritical CO<sub>2</sub> coupled with ethanol (EtOH) as co-solvent is of potential interest. This paper reports the experimental protocol followed, together with the kinetics of the extraction, the knowledge of which allows the optimization of working parameters and the determination of the process yields. Results obtained show that the proposed mathematical model is able to describe the extraction kinetics and that high percentages of EtOH ( $\geq 50\%$ ) need to obtain the extraction of whole polyphenolic pull.

## INTRODUCTION

Potato tubers contain a large number of phenolic compounds with antioxidant properties mainly found in the skin and in the periderm layer near to it. Among them, the most representative is the chlorogenic acid, which content ranges from 5 to 50 mg/kg of dry matter. Other phenolic substances include phenolic acids (caffeic, ferulic, protocatechuic and p-coumaric acids) and flavonoids (flavones, anthocyanidins) [1]. Due to their antioxidant power, potato phenolic compounds are considered relevant to prevent some human diseases and to promote the quality of life [2]. These natural antioxidants can be also extracted from potato by-products and used in food industry to prevent the decay by peroxidation of lipid bearing foods [3]. The recovery of these compounds requires the use of mild extraction technologies, in order to preserve the antioxidant power. In such a contest, the extraction with supercritical fluids (SFE) is of potential interest.

Within the Special Project “Natural vegetable antioxidants and food quality”, supported by the Italian Research Ministry (MIUR), an experimentation has been developed with the aim of testing the technical feasibility of a SFE process to recovery polyphenols from potato by-products. This paper reports the experimental protocol followed, together with the kinetics of the extractions, the knowledge of which allows the optimisation of working parameters and the determination of the process yields.

## I - MATERIALS AND METHODS

Potato tubers from Italian cv Desirè were supplied by the Dipartimento di Agronomia Ambientale e Produzioni Vegetali of the University of Padova, Italy. The skin with a thin periderm layer (total average thickness: 0.5-1.0 mm), collected from manually peeled tubers,

was washed, lyophilized and ground to a particle size of 37  $\mu\text{m}$ . Pure solvents and chemicals were used in the analyses, while commercial grade  $\text{CO}_2$  and ethanol (EtOH) were utilized in SFE.

SFEs were performed using a commercial pilot plant apparatus (SITEC, Maur, Switzerland), which allows the recovery and the subsequent recycling of the solvent, with a minimal loss of  $\text{CO}_2$ . A supplementary pump provides the addition of a co-solvent to the  $\text{CO}_2$  stream, when desired. The apparatus is detailed in a previous paper [4].

As a preliminary experimentation showed that pure supercritical  $\text{CO}_2$  (SC- $\text{CO}_2$ ) is a poor solvent for these polar compounds and that water is not suitable as co-solvent being unable to generate a homogeneous phase with SC- $\text{CO}_2$ , ethanol (EtOH) was considered and tested as co-solvent. It was used coupled to SC- $\text{CO}_2$  in a ratio of 50 % and 100% (w/w). In the experiment runs, EtOH showed a complete miscibility with SC- $\text{CO}_2$  and was quantitatively recovered in the separator. Extractions were carried out using 280 g of lyophilized matter per each run, with a working pressure (P) of 30 and 50 MPa and a temperature (T) of 50 and 80  $^\circ\text{C}$ . Because of different EtOH/SC- $\text{CO}_2$  ratios used, variable solvent flow rates were employed, while the extraction time was fixed in 80 min.

Extraction yields were determined gravimetrically, while the polyphenolic concentration in both extracts and lyophilized potato by-products was spectrophotometrically determined and expressed as chlorogenic acid [5].

Extraction of polyphenols by percolation with pure EtOH for 140 min was also performed using a Soxhlet apparatus (T = 52  $^\circ\text{C}$ ).

## II - RESULTS AND DISCUSSION

To optimise the extraction parameters, a kinetic approach developed during a previous research activity was adopted [5, 6]. This approach, based on the Fick's law, uses the following exponential equation to describe the evolution of extracted polyphenols over time (t):

$$Pe = H^* \cdot [Po] \cdot (1 - e^{-k \cdot t}) \quad (1)$$

were: Pe = grams of polyphenols extracted at a random time t per gram of biomass submitted to the extraction (adimensional);  $H^*$  = adimensional constant, ranging from 0 to 1, related to the equilibrium constant H ( $H^* = H/(H+1)$ ); [Po] = polyphenolic concentration in starting lyophilized material (adimensional); k = kinetic constant ( $\text{s}^{-1}$ ).

The extraction rate (R) calculated as first derivative of the equation 1:

$$R = dPe/dt = H^* \cdot [Po] \cdot k \cdot e^{-k \cdot t} \quad (2)$$

reaches its maximum value ( $R_{\text{max}}$ ) at the beginning of extraction, when t is closed to 0:

$$R_{\text{max}} = H^* \cdot [Po] \cdot k \quad (3)$$

According to Yu et al. [7], the value of  $R_{\text{max}}$  ( $\text{s}^{-1}$ ) was assumed as an index to evaluate the efficiency of the extraction system *versus* the polyphenolic fraction of potato by-products. In particular, while the constant k ( $\text{s}^{-1}$ ) gives information on the kinetics of the process, the adimensional product  $H^* \cdot [Po]$ , representing the asymptotic value of the extraction curve when  $t \rightarrow \infty$ , is a measure of the maximum amount of polyphenols extractable in the working

conditions adopted. In presence of a highly efficient extraction process,  $H^*$  tends to 1 and therefore the maximum amount of polyphenols extractable per unit of biomass is equal to the concentration of polyphenols in the starting material.

The identification of the best values to be assigned to the equation parameters  $H^* \cdot [Po]$  and  $k$  was carried out by a specific statistical program named BURENL<sup>®</sup> and described in a previous paper [8].

Table 1 reports the polyphenols extracted from potato by-products as a function of run time and working conditions adopted, while in Table 2 are reported the values assumed by  $R_{max}$  and by the functional parameters  $H^* \cdot [Po]$  and  $k$ .

**Table 1** – Amount of polyphenols extracted per unit of mass of potato by-product submitted to the extraction (mg/g) as a function of run time and working conditions (EtOH/CO<sub>2</sub> ratio, pressure and temperature). Data in the last column refer to the conventional extraction by percolation performed using a Soxhlet apparatus

Run time (min)	EtOH 50 % - CO <sub>2</sub> 50 %		EtOH 100 %		
	30 MPa		30 MPa	50 MPa	0.1 MPa
	50 °C	80 °C	80 °C	80 °C	52 °C
10	0.34	2.21	2.80	2.89	--
20	0.73	4.16	4.68	5.01	2.09
30	1.10	5.76	6.45	6.86	--
40	1.21	7.04	7.91	8.39	5.87
50	1.35	7.95	9.10	9.50	--
60	1.46	8.66	9.87	10.25	7.68
70	1.56	8.95	10.37	10.71	--
80	1.75	9.08	10.73	10.93	9.33
100	--	--	--	--	10.13
120	--	--	--	--	10.43
140	--	--	--	--	10.74

On the basis of data reported in Tables 1 and 2, the following remarks can be done: a) pure SC-CO<sub>2</sub> is a poor solvent for potato polyphenols, even when high values of pressure and temperature are adopted. In this case, in fact, more than density is the polarity of the solvent phase that plays a fundamental role in the extraction of these polar compounds; b) water is not suitable as co-solvent, being unable to generate a homogeneous phase with SC-CO<sub>2</sub>, at least in the range of water/SC-CO<sub>2</sub> tested (0.1 – 0.5); c) EtOH is a suitable co-solvent to pilot the polarity of solvent phase, but a high percentage ( $\geq$  al 50 %) needs to obtain high extraction yields; d) when working at the same EtOH/SC-CO<sub>2</sub> ratio (1:1) and pressure (30 MPa), temperature (T) highly affects the extraction process, with particular reference to the total amount of extractable polyphenols. In fact, while the kinetic constant  $k$  does not change markedly when T increases from 50 to 80 °C ( $3.92 \cdot 10^{-4} \text{ s}^{-1}$  and  $4.37 \cdot 10^{-4} \text{ s}^{-1}$ , respectively), the equation parameter  $H^* \cdot [Po]$  highly increases passing from  $1.739 \cdot 10^{-3}$  at 50 °C to  $9.055 \cdot 10^{-3}$

at 80 °C. This means that such increase in T determines the solubilization of phenolic compounds otherwise non collectable; e) to obtain the extraction of the whole phenolic fraction, pure EtOH at the temperature of 80 °C and at the pressure of 30 MPa (an increase of pressure to 50 MPa does not produce any appreciable increase) needs. In such conditions the extraction process is 1.5 times faster than that performed using the Soxhlet apparatus, as testify by the values assumed by the kinetic constant  $k$  ( $4.00 \cdot 10^{-4} \text{ s}^{-1}$  versus  $2.87 \cdot 10^{-4} \text{ s}^{-1}$ ); f) when EtOH decreases from 100 % to 50 %, only a little decrease in final extraction yield is obtained (83 % of total), probably due to a loss of the most polar phenolics, but the kinetics of extraction process remain substantially unchanged (see values of constant  $k$  in table 2).

**Table 2** – Value assumed by  $R_{\max}$  and by the equation parameters  $H^* \cdot [Po]$  and  $k$  as a function of working conditions adopted: T = temperature; P = pressure; i.c. = confidence interval ( $p = 0.05$ ). Data in the last row refer to the extraction by percolation performed using a Soxhlet apparatus. The samples of lyophilized potato by-product submitted to the extraction had a phenolic content of 1.09 % (w/w)

EtOH (%)	SC-CO <sub>2</sub> (%)	T (°C)	P (MPa)	$(H^* \cdot [Po] \pm \text{i.c.}) \cdot 10^3$ (adimensional)	$(k \pm \text{i.c.}) \cdot 10^4$ (s <sup>-1</sup> )	$(R_{\max} \pm \text{i.c.}) \cdot 10^6$ (s <sup>-1</sup> )
50	50	50	30	$1.739 \pm 0.010$	$3.925 \pm 0.088$	$0.682 \pm 0.018$
50	50	80	30	$9.055 \pm 0.011$	$4.375 \pm 0.031$	$3.961 \pm 0.033$
100	0	80	30	$10.817 \pm 0.013$	$4.000 \pm 0.025$	$4.326 \pm 0.033$
100	0	80	50	$11.209 \pm 0.011$	$4.394 \pm 0.021$	$4.925 \pm 0.028$
100	0	52	0.1	$10.940 \pm 0.008$	$2.872 \pm 0.019$	$3.142 \pm 0.023$

## CONCLUSION

Results obtained, together with the high values assumed by the correlation coefficient  $r$  (changed from a minimum of 0.994 to a maximum of 0.999), testify to the suitability of the hypotheses introduced and give a measure of the validity of the mathematical model proposed, which can be profitably utilised to completely describe the kinetics of an extraction process in general.

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