

1 **Ultrasound-assisted extraction of polyphenols from potato peels: Profiling and kinetic**  
2 **modelling<sup>†</sup>**

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27 **Abstract**

28 Ultrasound-assisted extraction (UAE) at 33 kHz and 42 kHz have been investigated in the extraction  
29 of polyphenols from peels of two potato varieties, cream-skinned Lady-Claire (LC) and pink-skinned  
30 Lady-Rosetta (LR), commonly used in snack-food production. Extraction efficacy between the UAE-  
31 untreated (control) and the UAE-treated extracts was assessed on the total phenolic content and  
32 antioxidant capacities (DPPH and FRAP). Application of UAE showed significantly higher recovery  
33 of phenolic compounds compared to solid-liquid extraction process alone. Lower ultrasonic frequency  
34 (33 kHz) was more effective in recovering polyphenols compared to 42 kHz ultrasonic treatment. The  
35 liquid chromatography-tandem mass spectrometry revealed that chlorogenic acid and caffeic acid  
36 were the most prevalent phenolics in LR peels, whereas caffeic acid was dominant in LC peels.  
37 Peleg's equation showed a good correlation ( $R^2 > 0.92$ ) between the experimental values and the  
38 predicted values on the kinetics of UAE of phenolic compounds.

39  
40 **Keywords:** Ultrasound-assisted extraction (UAE), potato peel, antioxidant activity (DPPH and  
41 FRAP), phenolic acids, UHPLC-MS/MS, Peleg's kinetics modelling

## 42 **1. Introduction**

43 Every year, tens of thousands tonnes of potato peels are generated by the snack-food industries  
44 worldwide and the peels are either used as cattle feed or disposed of in landfills that could cause  
45 environmental damage and disposal costs to the processors. However, potato peels have potential to  
46 be reutilised by exploiting them as sustainable source for high value food additives such as natural  
47 antioxidants (Rehman *et al.*, 2004), dietary fibre (Toma *et al.*, 1979) and anti-microbial agent (De  
48 Sotillo *et al.*, 1998). In particular, extracts from potato peel have exhibited potential as antioxidants in  
49 food systems (Kanatt *et al.*, 2005) due to their high content of polyphenols. Friedman (1997) reported  
50 that the polyphenols in potato peel, which accounted for approximately 50% of all polyphenols in  
51 potato tuber, are ten times higher than in the pulp. These polyphenols exhibit natural antioxidant  
52 capacities by scavenging reactive oxygen species (ROS) i.e. free radicals (through electron or  
53 hydrogen atom transfers) thus inhibiting oxidative damages to the cell components. However, in food  
54 application (mainly for stability of lipids and fats) they stabilise the free radicals through resonance  
55 delocalisation instead of terminating peroxy free radicals by donating hydrogen atom as done by  
56 commercial antioxidants (Tiwari *et al.*, 2013). They could be a potential replacement of synthetic  
57 antioxidants such as butylated hydroxyanisole and butylated hydroxytoluene and tertiary  
58 butylhydroquinone (have shown some evidence of toxic and carcinogenic properties (Branen, 1975)),  
59 in food preservation as well as food fortification.

60 In recent years, a number of improved novel extraction methodologies including ultrasound-assisted  
61 extraction (UAE) have emerged as efficient extraction alternatives to conventional extraction  
62 techniques. Advantages of UAE include simplicity, flexibility, versatile, easy to use, requiring  
63 relatively low capital investment and scalable for commercial uses (Patist and Bates, 2008).  
64 Essentially, the ultrasonic treatment amplifies extraction efficiency by accelerating diffusion,  
65 improving solvent penetration and increased mass transfer. UAE has been reported to be efficient for  
66 the recovery of diverse range of valuable compounds such as polysaccharides, pectin, hemicellulose,  
67 proteins, unsaturated fatty acids, glycoalkaloids and phenolic compounds (Chen *et al.*, 2011, Samaram  
68 *et al.*, 2015, Tabaraki and Nateghi, 2011, Karki *et al.*, 2010, Fu *et al.*, 2006). In addition studies  
69 investigating the ability of UAE to enhance yields of polyphenols from food waste published to date

70 have used HPLC or TLC to characterise phenolic compounds (Wijngaard *et al.*, 2012, Onyeneho and  
71 Hettiarachchy, 1993), which suffer from specificity and low sensitivity in detecting target molecules.  
72 On contrary, employing ultra-high performance liquid chromatography tandem mass spectrometry  
73 (UHPLC-MS/MS) will confer a greater specificity, sensitivity and speed to polyphenol analysis. In  
74 addition the modelling of extraction kinetics helps in predicting the optimum extraction parameters to  
75 recover maximum target molecules from plant matrices. Peleg's model of sorption kinetics (Peleg,  
76 1988) has been applied for various UAE kinetic studies like chicory by-products (Pradal *et al.*, 2016),  
77 bioactives from brown seaweed (Kadam *et al.*, 2015), however this approach has not been adopted  
78 from the UAE recovery of polyphenols from potatoes. In present study, we have investigated the  
79 effect of UAE on the kinetic of extraction of phenolic compounds from potato peel of two different  
80 potato varieties collected from snack-food manufacturing industries followed by UHPLC-MS/MS  
81 characterisation.

## 82 **2. Material and methods**

### 83 **2.1 Materials and reagents**

84 Phenolic standards chlorogenic acid, caffeic acid, trans-cinnamic acid, gallic acid, ferulic acid,  
85 isoferulic acid, rutin, protocatechuic acid, luteolin-7-*O*-glucoside and p-coumaric acid, all other  
86 chemicals and HPLC-grade organic reagents were purchased from Sigma-Aldrich (Wicklow, Ireland).  
87 The enzymes  $\alpha$ -amylase, protease and amyloglucosidase were purchased from Megazyme (Wicklow,  
88 Ireland).

### 89 **2.2 Sample preparation**

90 Potato peels slurry arising from two potato varieties namely Lady-Claire (LC) and Lady-Rosetta (LR)  
91 were provided by Largo Foods Limited (Meath, Ireland). Freeze-drying was carried out for the  
92 stability of the raw material on the frozen peel in FD 80 GP "LEANNE" freeze drier model  
93 (CUDDON Limited, New Zealand) at a temperature of -50 °C and a pressure of 0.01 mbar for 24 h.  
94 Freeze dried samples were immediately powdered, vacuum packed and kept in -20 °C for further  
95 analysis.

### 96 **2.3 Proximate analysis of potato peel powder**

97 The protein content was measured using a nitrogen analyser (FP-628 Leco Instrument, USA) based on  
98 the Dumas principle ( $N \times 6.25$ ), total fat using acid hydrolysis method (AOAC 954.02), ash content  
99 by AOAC 923.03 method (AOAC., 2000) and total carbohydrate was calculated by difference i.e.  
100  $[100 - (g \text{ protein} + g \text{ fat} + g \text{ ash})]$ . Total dietary fibre analysis of LC potato peel was conducted by  
101 ANKOM automated dietary fibre analyser in accordance with the AOAC (1990) method 991.43.

## 102 **2.4 Generation of crude phenolic extracts**

### 103 **2.4.1 Solid-liquid extraction (SLE)**

104 A preliminary solid-liquid extraction was carried out on peels from LR variety using different solvent  
105 combinations, i.e. 1) 100% distilled water, 2) 100% methanol, 3) 80% methanol-water and 4) 50%  
106 methanol-water (v/v) to select the best solvent combination for extraction of phenolic compounds  
107 from potato peel. The polyphenol content from SLE was used to benchmark the effect of UAE on  
108 various parameters of the extracts in addition to potato varietal comparison. Briefly, dried and ground  
109 potato peel samples (2 g) were extracted with 20 mL of solvents at room temperature ( $\sim 23^\circ\text{C}$ ) for  
110 overnight (15 h) in a tube shaker at 1500 rpm (Multi Reax, Heidolph, UK). The resulting slurries were  
111 then centrifuged for 10 min at 4000g. The supernatant was immediately filtered using a  $0.45 \mu\text{m}$   
112 PTFE syringe filter and stored at  $-20^\circ\text{C}$  until further analysis. Two replicate extractions were carried  
113 out per sample.

### 114 **2.4.2 Ultrasound-assisted extraction (UAE)**

115 Freeze dried potato peel powders (1 g) mixed with 80% methanol at a fixed ratio of 1:10 (w/v) were  
116 subjected to UAE for 30, 60, 180, 360, and 900 min in separate tubes. Ultrasonic treatment was  
117 carried out by submerging the tubes (four tubes per treatment time) in ultrasonic bath BRANSON  
118 3510 with operating frequency of 42 kHz (45 W). Another ultrasonic bath JENCONS S1000  
119 operating at 33 kHz (100 W) was used only with LC variety to understand the effect of ultrasonic  
120 frequency/power on the extraction of phenolic compounds of potato peel. The temperature of the  
121 samples during sonication treatment was monitored using thermocouples (Radionics, Ireland), which  
122 ranged from (30 to 45)  $^\circ\text{C}$ . The extracts were collected and stored at  $-20^\circ\text{C}$  until further analysis.

## 123 **2.5 Phenolic content and antioxidant activity**

124 The total phenolic content (TPC) and two antioxidant assays, namely DPPH radical scavenging and  
125 FRAP reducing power capacity, were determined by colourimetric assays. The TPC of extracts was  
126 estimated by using the Folin-Ciocalteu reagent as described by Singleton and Rossi (1965); Gallic  
127 acid solutions of different concentrations (10-100 µg/mL) were used to prepare calibration curve and  
128 the results were expressed as milligram of gallic acid equivalent per gram dry weight basis (mg  
129 GAE/gdb). The 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay was performed using a modified  
130 version of the method proposed by Goupy *et al.* (1999); Various Trolox concentrations (1-8 µg/mL)  
131 were used for standard curve and the activity was expressed as milligram equivalents of Trolox per  
132 gdb (mg TE/gdb). FRAP activities were carried out based on the procedure of Stratil *et al.* (2006);  
133 Calibration curve consisting of different Trolox concentrations (25-150 µg/mL) was prepared and the  
134 results were also expressed as mg TE/gdb. All the experiments were performed in duplicate and the  
135 results were expressed as mean ± standard deviation (SD).

## 136 **2.6 UHPLC-MS/MS analysis of polyphenols**

137 Mass spectrometry analysis of the potato peel polyphenols was performed as described by  
138 Gangopadhyay *et al.* (2016) with some modifications. The filtered methanolic extracts of potato peels  
139 were first screened against 55 known polyphenols from an 'in-house' database using an Acquity ultra-  
140 high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) (Waters  
141 Corp., MA, USA). Following the identification against authentic standards, the multiple reaction  
142 monitoring (MRM) transitions of the detected polyphenols were used for quantification purpose  
143 (Supplementary Table S1). Separation of the analytes was achieved on a HSS T3 (C18 column, 2.1 x  
144 100 mm, 1.8 µm) using the solvents 0.1% formic acid in water (solvent A) and 0.1% formic acid in  
145 acetonitrile (solvent B) with following gradient: 0-1 min, 2% B; 1-2.5 min, 10% B; 2.5-6 min, 15% B;  
146 6-7.5 min, 50% B; 7.5-9.5 min, 98% B and 9.5-10 min, 2% B at a rate of 0.5 mL/min. The UHPLC-  
147 MS/MS data were acquired using electrospray ionisation in negative ion mode with following  
148 ionisation conditions: capillary voltage 3 kV, cone voltage 30 V, extractor voltage 3 V, source  
149 temperature 120 °C, and desolvation temperature 250 °C. Calibration curves were prepared using 0.1  
150 to 1 µg/mL concentration range for each phenolic compound except for chlorogenic acid and caffeic  
151 acid. Chlorogenic acid standards were prepared in the range of 0.1-15 µg/mL whereas caffeic acid

152 standards were between 1-10 µg/mL. The concentration of each phenolic compound in the sample  
153 was quantified using the TargetLynx software (Waters Corp., MA, USA).

## 154 **2.7 Extraction kinetics and statistical analysis**

155 A two-parameter, non-exponential Peleg's sorption kinetic model was employed to describe the  
156 extraction kinetics of total phenolic concentration and individual phenolic components (chlorogenic  
157 acid and caffeic acid) as a function of potato peel variety and ultrasonic frequency:

158

$$C(t) = C_0 + \frac{t}{K_1 + K_2 \cdot t} \quad (1)$$

159 Where,  $C(t)$  is the concentration/bioactivity of targeted compound at time  $t$  (min),  $C_0$  is the initial  
160 concentration/activity at time  $t = 0$  (mg /gdb),  $K_1$  is Peleg's rate constant and  $K_2$  is Peleg's capacity  
161 constant. Since  $C_0$  in all experimental case was zero, so equation (1) was modified as follows (Eq. 2)  
162 for experimental data approximation i.e. predicted values.

$$C(t) = \frac{t}{K_1 + K_2 \cdot t} \quad (2)$$

163

164 The Peleg's rate constant  $K_1$  relates to the extraction rate ( $B_0$ ) at the start ( $t = t_0$ ).

$$B_0(\text{mg/g}_{\text{db}}) = \frac{1}{K_1} \quad (3)$$

165 The Peleg's capacity constant  $K_2$  relates to the extraction extent ( $C_e$ ) at equilibrium ( $t = \infty$ )

$$C_e(\text{mg/g}_{\text{db}}) = \frac{1}{K_2} \quad (4)$$

166 Analysis of variance was carried out using SAS, USA Version 9.3 statistical software. Nonlinear  
167 regression was used to determine the two parameters of Peleg's model i.e. constant  $K_1$  and  $K_2$  using  
168 non-linear regression (Gauss-Newton method). Model fitting was judged based on regression  
169 coefficient ( $R^2$ ).

## 170 **3. Results and discussion**

### 171 **3.1 Proximate composition**

172 The proximate composition results of peels from two potato cultivars (Table 1) were broadly within  
173 the range of previously reported values for potato peels (Amado *et al.*, 2014, Camire *et al.*, 1997)  
174 except for the fat content, where these authors have observed slightly lower levels (0-1.07%) with  
175 respect to our data, i.e. 1.27-2.09% fat. These variations in potato peel composition may be attributed  
176 to various factors including varietal differences, peeling techniques, agronomic and other  
177 environmental factors (Burlingame *et al.*, 2009, Camire *et al.*, 1997). The protein and carbohydrate  
178 content were significantly higher ( $p < 0.05$ ) in Lady Claire (LC) peels compared to the Lady Rosetta  
179 (LR) peels. The LC variety contained ~ 51% total dietary fibre presenting it as an attractive and  
180 sustainable source of dietary fibre.

### 181 **3.2. Extraction efficacy of solvent combination for polyphenols**

182 Several studies have used methanol to extract polyphenolic compounds from potato peels (Mohdaly *et*  
183 *al.*, 2010, Singh *et al.*, 2011, Singh and Saldaña, 2011). However a combination of water and alcohol  
184 (ethanol, methanol) has shown better extraction efficiency compared to organic solvents alone. For  
185 example, Turkmen *et al.* (2006) have reported the lowest total polyphenols (23.5 mg GAE/gdb) with  
186 absolute methanol, however the highest level of polyphenol (82.3 mg GAE/gdb) was noted with 50%  
187 methanol in black tea. Similarly Zhou and Yu (2004) on using 70% ethanol led to higher recovery of  
188 total phenols compared to ethanol alone from wheat bran. Yu *et al.* (2005), also observed that 80%  
189 methanol and 80% ethanol resulted in approximately 60% higher TPC from peanut skins when  
190 compared to water alone. Lapornik *et al.* (2005), on the other hand, used 70% alcohol (methanol or  
191 ethanol) and observed 2-4 fold increase in polyphenols and anthocyanins recovery after 12 h of  
192 extraction from red-current and black-current by-products compared to water alone. Hence various  
193 combinations of water-methanol for the extraction of potato peel polyphenols were investigated  
194 (Supplementary Table S2). Examination of the data revealed that use of an 80% methanol-water  
195 resulted in significantly higher ( $p < 0.05$ ) level of TPC and antioxidant activity compared to other  
196 combinations examined. Findings by other authors and this study clearly suggested that the  
197 polyphenols extraction is improved using methanol-water combination, and therefore the 80%  
198 methanol was used as extractant to examine the effect of ultrasound treatment on phenolic yield in the  
199 peels.



### 200 3.3 Antioxidant activities and phenolic content of potato peel SLE extracts

201 As shown in Table 2, levels of total phenolic content (2.17-3.28 mg GAE/gdb) are within the range of  
202 those reported previously by other authors [Al-Weshahy and Venket Rao (2009) (1.51-3.33 mg  
203 GAE/gdb, Mohdaly *et al.* (2010) (2.91 mg GAE/gdb)]. It is also evident that LR peel possesses  
204 significantly higher ( $p < 0.05$ ) amount of total phenolics and antioxidant activities compared to LC  
205 variety. One possible reason for a higher level of phenolics in LR peels is probably due to its  
206 pigmented skin as studies have shown that coloured potatoes have higher phenolic contents compared  
207 to white or brown-skinned potatoes (Lachman *et al.*, 2008, Al-Weshahy and Venket Rao, 2009). The  
208 high antioxidant activity from LR peels is supported by the fact that total phenolic content (TPC) and  
209 antioxidant activity (DPPH and FRAP) exhibited significantly high correlation for both the activities  
210 ( $r > 0.99$ ,  $p < 0.05$ ). This is further supported by the UHPLC-MS/MS data where the total phenolic  
211 acids (sum of chlorogenic acid and caffeic acid) in LR and LC were 322.4  $\mu\text{g/gdb}$  and 70.4  $\mu\text{g/gdb}$ ,  
212 respectively (Table 2). This shows that antioxidant activity is influenced by the amount of phenolics  
213 extracted vis-a-vis varieties employed for extraction. Similar correlations haven been observed by  
214 Amado *et al.* (2014) in the phenolic compounds and antioxidant activities of 'Agria' potato peel.  
215 As identified and quantified using UHPLC-MS/MS (Supplementary Figure S1), chlorogenic acid  
216 (23.7 mg/100gdb) and caffeic acid (8.5 mg/100gdb) were the two predominant phenolic acids in LR  
217 peel whereas caffeic acid (6.8 mg/100gdb) was the prevalent phenolic acid in LC (Table 2). Minor  
218 peaks of ferulic acid, p-coumaric acid, vanillic acid and rutin were also identified, however these  
219 compounds were present at levels below the limit of quantification for the method applied. Wijngaard  
220 *et al.* (2012) have also shown that the caffeic acid is the predominant phenolic acid in LC peel,  
221 however the maximum content reported was 65.1 mg/100gdb. This significant variation may be  
222 attributed to the choice of peels, method of extraction and analysis, agronomical or environmental  
223 factors. The relative abundance of chlorogenic acid is in line with previous studies as the most  
224 prevalent phenolic acid in potato peel (Onyeneho and Hettiarachchy, 1993, Nara *et al.*, 2006, Singh *et*  
225 *al.*, 2011, Singh and Saldaña, 2011). Al-Weshahy and Venket Rao (2009) found that chlorogenic acid  
226 (2.79 mg/gdb) in red colour potato peel from si cle variety was the highest among all the other five

227 varieties used in their study followed by caffeic acid (0.26 to 0.72 mg/gdb). In another study, Nara *et*  
228 *al.* (2006) identified two major peaks of chlorogenic acid and caffeic acid in potato peel extracts as  
229 free polyphenols and reported low levels of ferulic acid (0.37  $\mu$ mol/gdb) in bound extracts. The type  
230 of polyphenols detected and their amounts measured in the present study varied from the above  
231 referred studies demonstrating the natural variation of polyphenols content due to different agronomic  
232 factors, varietal differences or different processing practices.

### 233 **3.4 Effect of ultrasonic treatment on phenolic components of potato peels**

234 The total phenolic content (TPC), antioxidant activity and individual phenolic acids in ultrasound  
235 treated potato peel extracts were significantly higher ( $p < 0.05$ ) than in SLE extracts alone (Table 2).  
236 The TPC levels in SLE extracts increased from 3.28 mg GAE/gdb to 7.67 mg GAE/gdb in the LR  
237 variety whereas for LC variety the TPC increased from 2.17 mg GAE/gdb to 4.24 mg GAE/gdb  
238 following ultrasonication treatments. Similarly, UAE extracts had almost doubled the DPPH radical  
239 scavenging activity and a 3.5 fold higher FRAP capacity compared to SLE extracts for these two  
240 potato peel varieties. These findings are similar to other studies where the potentials of UAE for the  
241 extraction of phenolics and antioxidants from agro-industrial wastes have been explored. Khan *et al.*  
242 (2010) have demonstrated that UAE extraction of total phenols from orange peel was approximately 3  
243 times faster with 35–40% increase in TPC compared to conventional solvent extraction. They have  
244 also reported considerably higher recovery of naringin (70.3 mg/100g of fresh weight) and hesperidin  
245 (205.2 mg/100g of fresh weight) from UAE than those obtained from conventional extraction (50.9  
246 and 144.7 mg/100 g fresh weight, respectively) from orange peels. Another study by Ma *et al.* (2009)  
247 have demonstrated improved extraction efficiency of phenolic compounds such as caffeic and p-  
248 coumaric acid (4 fold), ferulic acid (6 fold), sinapic acid (5 fold), p-hydroxybenzoic acid and vanillic  
249 acid (2 fold) from citrus peel using UAE in contrast to a conventional maceration extraction  
250 technique using the same extraction time (1 h) and temperature (40 °C). The greater efficiency of  
251 UAE may be attributed to the mechanical effects arising from cavitation phenomenon and strong  
252 micro-streaming currents development due to ultrasound wave (Soria and Villamiel, 2010). Acoustic  
253 cavitation followed by cavitation dislodgment together with micro-jetting and micro-streaming  
254 effects, causes disintegration of solid materials, disruption of cell walls and greater penetration of

255 solvents leading to increased diffusion rate and thereby accelerating the mass transfer (Vinatoru *et al.*,  
256 1997).

257 In addition, the effect of ultrasonic frequency/power on the recovery of phenolic compounds and  
258 corresponding antioxidant activity were studied using the LC variety peel. As can be seen in Table 2,  
259 using the lower frequency (higher output power) of 33 kHz (100 W) as compared to the higher  
260 frequency (lower output power) of 42 kHz (45 W) resulted in the total phenolic content, chlorogenic  
261 acid concentration and DPPH antioxidant activity increasing significantly ( $p < 0.05$ ) from 3.8 to 4.24  
262 mg GAE/gdb, 5.98 to 8.69 mg/gdb and 3.16 to 3.66 mg TE/gdb, respectively. However, no significant  
263 differences were observed for caffeic acid concentration and FRAP antioxidant activity. The reason  
264 for this is unclear. However results for other indices of extraction efficiency clearly exhibited that  
265 lower ultrasonic frequency was more effective compared to higher frequency. Similar findings were  
266 reported for polyphenol recovery using ultrasonication from spinach (Altemimi *et al.*, 2015), where  
267 the ultrasonic bath operating at 37 kHz was more effective than 80 kHz at temperature-power-time  
268 combination of 40 °C, 50% and 30 min, with regard to extraction yield, total phenols and % DPPH  
269 inhibition. Furthermore, higher intensity/power ultrasound effectiveness over lower intensity/power  
270 has also been testified for recovery of protein from soy flakes (Karki *et al.*, 2010) and glycoalkaloids  
271 from potato peel (Hossain *et al.*, 2014).

272 Higher phenolic yield and antioxidant activity at a lower frequency may be associated with increased  
273 intensity of acoustic cavitation in the solvent medium as cavitation intensity is inversely related to  
274 ultrasonic frequency. It is also evident from literature that ultrasonic frequency is one of the  
275 significant factors affecting acoustic cavitation (Tiwari, 2015). Improved extraction efficiency at  
276 lower frequency may be linked to the generation of larger but relatively fewer cavitation bubbles  
277 which implode with higher energy level thus resulting in a greater degree of cell disruption (Wu *et al.*,  
278 2013).

### 279 **3.5 UAE kinetics of potato peel and Peleg's model**

280 Figures 1a to 1c show the kinetic profile of phenolic extraction for each UAE treatment fitted by  
281 Peleg's model. The path of extraction curves indicate similarity with sorption process kinetics  
282 described by Peleg's model. It can be observed that time has significant positive effect on the extent

283 of bioactive extraction. The rate of extraction was higher at the start of the extraction which plateaus  
284 towards the end of treatment time.

285 The obtained constants of Peleg's model (rate constant  $K_1$ , capacity constant  $K_2$ ) and calculated  
286 parameters, i.e. regression coefficient ( $R^2$ ), initial extraction rate ( $B_0$ ) and extraction extent ( $C_e$ ), are  
287 shown in Table 3. The high regression coefficients ( $R^2 > 0.921$ ) in all the studied conditions and  
288 corresponding graphs indicate good agreement between experimental values and predicted values  
289 calculated using Peleg's equation proving well fit of this model. This implies that the Peleg's equation  
290 can be used to predict the phenolic extraction under different ultrasonic frequencies at a given time.  
291 Jokić *et al.* (2010) have applied the Peleg's model to describe the kinetics of solid-liquid extraction  
292 process of total polyphenols from soybeans. The authors reported that all the experimental data well  
293 fitted with the model's calculated data with correlation coefficient ( $r$ ) ranging between 0.985-0.994  
294 indicating the suitability of Peleg's model for the purpose of optimising the solid-liquid extraction  
295 process for polyphenols. Galván D'Alessandro *et al.* (2014) have confirmed the kinetic model for  
296 optimised UAE of anthocyanin from black chokeberry wastes with good agreement between  
297 experimental data and the predicted data.

#### 298 **4. Conclusions**

299 The potato peel slurry from two different potato varieties, Lady-Claire (LC) and Lady-Rosetta (LR),  
300 produced as by-products of industrial processing could be a sustainable source of antioxidant  
301 polyphenolic compounds namely chlorogenic acid and caffeic acid. Chlorogenic acid is the dominant  
302 phenolic in LR peel whilst caffeic acid is the principal phenolic acid in LC peel. An 80% aqueous  
303 methanol is the most suitable solvent for extraction of phenolics from potato peels. The use of UAE  
304 significantly improves the recovery of antioxidant rich polyphenolic extract compared to conventional  
305 extraction methods alone. Lower ultrasonic frequency (33 kHz) treatment was more efficient in  
306 extraction than the higher frequency treatment (42 kHz). LR potato peel extracts had higher phenolic  
307 content (7.67 mg GAE/gdb) and higher antioxidant activity (DPPH value 5.86 mg TE/gdb, FRAP  
308 22.21 mg TE/gdb) compared to LC peel and therefore would be a preferred choice of natural  
309 antioxidants for food preservation and/or functional food ingredient applications. The use of Peleg's

310 model of diffusion ( $R^2 > 0.92$ ) served valuable tool for understanding the kinetics of ultrasound aided  
311 extraction to predict the phenolic yield of the extracts under varied range of extraction time.

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## 316 **6. Competing interests**

317 The authors declare that they have no competing interests.

318

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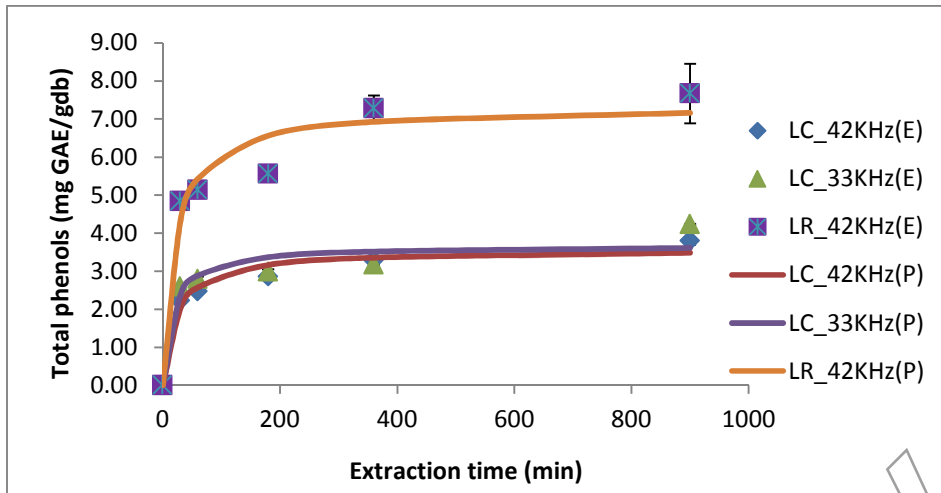
440 **Legends to Figures**

441 Figure 1. Experimental (E) and predicted (P) extraction kinetics of potato peels fitted by Peleg's  
442 model for polyphenols: (a) total phenolics; (b) chlorogenic acid; and (c) caffeic acid.

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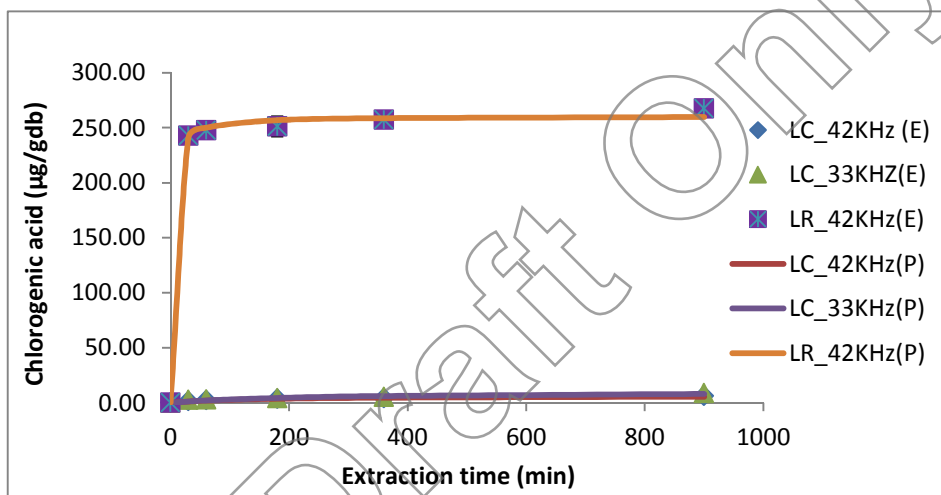
443 **figure 1**

444 a)



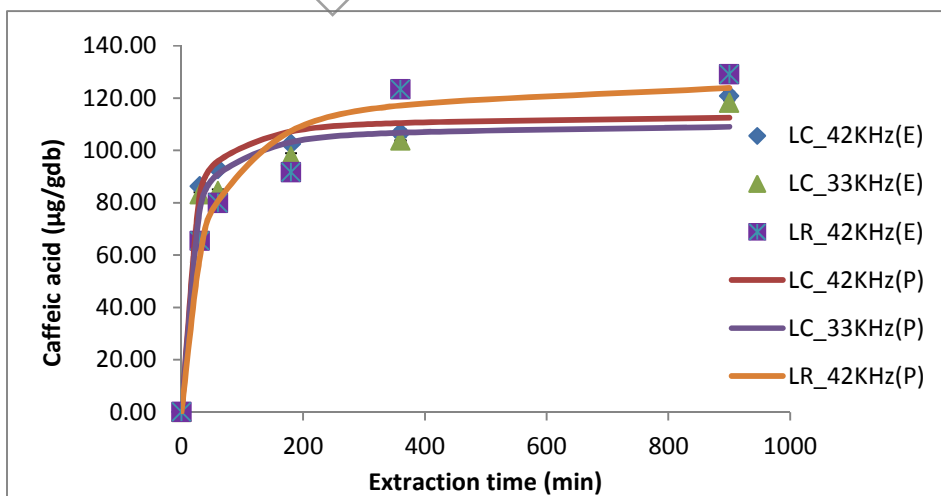
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446 b)



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448 c)



449

450 **Table 1.** Proximate composition of potato peel powder in Lady Rosetta (LR) and Lady Claire (LC)  
451 cultivars

Parameters	% dry wt. (LR)	% dry wt. (LC)
Crude fat	2.09 ± 0.01 <sup>a</sup>	1.27 ± 0.38 <sup>a</sup>
Crude protein	11.17 ± 0.03 <sup>b</sup>	12.44 ± 0.09 <sup>a</sup>
Ash	7.24 ± 0.02 <sup>a</sup>	4.83 ± 0.13 <sup>b</sup>
Moisture	6.98 ± 0.05 <sup>a</sup>	4.08 ± 0.04 <sup>b</sup>
Total Carbohydrate	72.53 ± 0.08 <sup>b</sup>	77.38 ± 0.65 <sup>a</sup>

452 Each value is expressed as mean ± standard deviation (n=2)

453 Means with different letters within a row are significantly different ( $p < 0.05$ )

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454 **Table 2.** Phenolic composition of 80% methanolic extracts from potato peel derived from two  
 455 varieties of potato

Extraction condition	Potato peel variety	Total Phenol (mg GAE/gdb)	DPPH activity (mg TE/gdb)	FRAP activity (mg TE/gdb)	Chlorogenic acid ( $\mu$ g/gdb)	Caffeic acid ( $\mu$ g/gdb)
SLE	LR	$3.28 \pm 0.07^{*,\$}$	$3.51 \pm 0.00^{*,\$}$	$6.27 \pm 0.06^{*,\$}$	$237.36 \pm 6.15^{*,\$}$	$85.08 \pm 0.47^{*,\$}$
	LC	$2.17 \pm 0.02^{*,a}$	$1.75 \pm 0.05^{*,a}$	$3.45 \pm 0.10^{*,a}$	$2.16 \pm 0.20^{*,a}$	$68.19 \pm 0.52^{*,a}$
UAE/ 42 kHz	LR	$7.67 \pm 0.79^{\$}$	$5.86 \pm 0.09^{\$}$	$22.21 \pm 0.24^{\$}$	$267.4 \pm 6.97^{\$}$	$129.05 \pm 0.97^{\$}$
	LC	$3.80 \pm 0.09^b$	$3.16 \pm 0.05^b$	$5.85 \pm 0.11^b$	$5.98 \pm 0.27^b$	$120.83 \pm 1.63^b$
UAE/ 33 kHz	LC	$4.24 \pm 0.01^c$	$3.66 \pm 0.00^c$	$5.64 \pm 0.05^b$	$8.69 \pm 0.38^c$	$118.28 \pm 0.97^b$

456 <sup>\*</sup> denotes significant difference ( $p < 0.05$ ) within a column, relative to SLE treatment between the variety

457 <sup>\\$</sup> denotes significant difference ( $p < 0.05$ ) within a column, relative to LR variety between extraction conditions

458 <sup>abc</sup> letters followed by different alphabet within a column are significantly different ( $p < 0.05$ ), relative to LC

459 variety among extraction conditions

460 **Table 3. Peleg's model constants ( $K_1$  and  $K_2$ ), initial extraction rate ( $B_0$ ) and extraction extent**  
 461 **( $C_e$ ) for UAE extracts with regression coefficients**

Bioactives	UAE variable	$K_1$ (min. gdb/mg or $\mu$ g)	$K_2$ (gdb/mg or $\mu$ g)	$B_0$ (mg or $\mu$ g/gdb)	$C_e$ (mg or $\mu$ g/gdb)	$R^2$ (Regression coefficient)
Chlorogenic acid ( $\mu$ g/gdb)	LC_33 kHz	22.853	0.100	0.044	10.030	0.921
	LC_42 kHz	22.241	0.155	0.045	6.460	0.969
	LR_42 kHz	0.010	0.004	104.004	260.417	0.998
Caffeic acid ( $\mu$ g/gdb)	LC_33 kHz	0.117	0.009	8.514	110.619	0.977
	LC_42 kHz	0.099	0.009	10.106	113.960	0.986
	LR_42 kHz	0.278	0.008	3.594	128.866	0.968
TPC (mg GAE/gdb)	LC_33 kHz	4.476	0.272	0.223	3.677	0.930
	LC_42 kHz	6.507	0.280	0.154	3.573	0.972
	LR_42 kHz	2.840	0.137	0.352	7.310	0.954

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