

# Kinetics of Potassium Diffusion as Influenced by Microstructure of Potato

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**Abstract** The effect of microstructure and temperature on the mechanism of potassium diffusion through and out of potato was studied at 15-120°C by means of the scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and leaching experiments. Tissues from different regions of the same tuber differed in their microstructural architecture and response to heat. The water-rich perimedullary region showed a regular and more defined arrangement of cells with larger vacuoles than the cortex which had irregularly arranged cells with densely packed starch granules. Granule morphology remained visibly unchanged at temperatures below 50°C. The gelatinization temperatures and range were significantly higher in the perimedullary. In addition, the average transition enthalpy was about 3 J/g lower in the perimedullary. The different microstructural architecture and thermal properties of tissues from different regions of the same tuber were linked with different membrane permeabilities and solubility with implications for the rate and mechanism of potassium transport through and out of potatoes.

**Keywords:** leaching, pre-heating, gelatinization, scanning electron microscopy, differential scanning calorimetry

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## 1. Introduction

Potato supplies nutritious food more quickly on less land and harsher climatic conditions than any other major crop. Over 85% of the plant is edible human food compared with the 50% for cereals [1]. The rising health awareness and quest for novel functionality have resulted in increased demand for the production of potato-based foods with promising health benefits [2].

Potato offers one of the most affordable sources of potassium with potassium level per fresh weight (280-564 mg/100g) considerably higher than banana, oranges, mushroom, milk, avocados, raisins, orange, salmon, spinach and tomatoes [3,4]. Potato supplies 18% of the total potassium intake of Brits, followed by meat and meat products (15%), dairy products (13%), cereals and cereal products (13%) and vegetables (10%) [5]. Potassium is a major constituent of fruits, vegetables and meat. Consequently, the option of a potassium-free diet is virtually impossible. Until now, dietary management of renal diseases has and continues to focus chiefly on avoidance or severe restriction of potassium rich food stuffs (> 250 mg/100 g). The patients are therefore placed on stringent dietary restrictions to limit their daily intake to within 1.7 mg to 2.5 mg range [6,7,8,9].

The main mechanism of solute transport or extraction in potato during blanching is by diffusion. Whilst it has been suggested that diffusion through a solid matrix does not occur and that, what happens is diffusion in the liquid

contained within the matrix or diffusion via the gas phase in a porous solid [10], it has been argued that diffusion through cellular walls and membranes do occur [11,12]. It has been demonstrated that diffusion increases significantly when potato tissue is preheated. This may be due to a denaturation of the cell walls and membranes, acting as an ultra filtration membrane, allowing water, sugars, and salts to diffuse freely in the tissue [13,14,15].

The diffusion coefficient, a fundamental parameter in Fick's law, is commonly applied, under set assumptions, to evaluate and model mass transfer processes (drying, lixiviation, absorption, permeation etc.) in foods. The assumptions (including negligible external resistance to mass transfer, negligible internal and external heat transfer effects and no shrinkage) are made to make the models simpler and thus easier to solve. Nonetheless, significant variation in the magnitude of calculated effective diffusivities for the same material and process have mainly been attributed to structural changes in the food material during the different stages of the diffusion process [16,17,18]. Whilst the involvement of chemical, physical and structural changes during heat treatments of potato tissue is common knowledge, the nature, degree and mechanism of the associated modifications have not been fully explored. The reliability of the calculated values of the effective diffusivity is dependent on the model's ability to accurately capture these changing dynamics of the mass transfer process.

Gelatinization, which describes the collapse of molecular orders within the starch granule, manifests itself in irreversible changes in properties including granular

swelling, native crystalline melting, loss of birefringence, and starch solubilisation [19]. Studies involving small- and wide-angle X-ray scattering, small-angle neutron scattering and Differential scanning calorimetry (DSC) have confirmed that when starch is heated in the presence of water, penetration of water into the amorphous regions occurs with swelling of the granule which strip starch chains from the surface of the ordered crystallites, effectively breaking the crystallites apart and generating an endotherm in the gelatinization process. As a process, gelatinization imposes different microstructural changes on the potato starch, a major constituent of the tissue, which in turn affect the diffusion dynamics of potassium in potatoes. Although many studies on the gelatinisation of starch in foods have focussed on the use of starch extracts [20, 21], most cooking involve the use of fresh potatoes. It is ideal that the thermal properties of potatoes which relate to the diffusion of potassium through and out of the potato tissues are studied in situ.

This study was, therefore, undertaken to gain a deeper understanding of the effect of microstructural architecture and heat-induced microstructural modifications on the mechanism of potassium diffusion through and out of potatoes.

## 2. Material and Methods

### 2.1. Materials

An oval-shaped, medium sized (6-8 cm diameter) potato (*Solanum tuberosum*) of the Estima variety was obtained from a local Sainsbury supermarket (UK). This light yellow-skinned, second most popular, potato in the UK was selected based on its all year-round availability, consumption level and regular shape. The potatoes, grown in Norfolk and Shropshire in the UK, were stored in the laboratory at room temperature and analysed within five days of purchase. Tubers were washed under running water, wiped with blotting paper and hand peeled with a stainless steel vegetable peeler. They were cut with a kitchen knife into 2.0 cm cubes. Dimensions were checked using a vernier calliper correct to 0.025 cm. The moisture content of samples was determined using the oven dry method.

### 2.2. Scanning Electron Microscopy (SEM)

The cellular structures of the potato tissues from different zones of the tuber were studied at 15-80°C. Micrographs of the raw and preheated samples were captured with the JOEL JSM-6060LV scanning electron microscope (Oxford Instruments, Abingdon, England). The freeze dried samples were adequately coated with graphite by low-vacuum sputtering and micrographed at an accelerating potential of 15 keV.

### 2.3. Differential Scanning Calorimetry (DSC)

The gelatinization parameters were measured with a DSC 1 STAR<sup>c</sup> System (Mettler-Toledo AG, Schwerzenbach, Switzerland) equipped with a thermal analysis data station and data recording software. In a pre-weighed 40  $\mu$ L aluminium pan, samples of potato tissues from the cortex

and perimedullary regions were weighed and hermetically sealed. The lid of the sample pan was pierced with a pin and crimped for DSC analysis. Samples were run under nitrogen flow rate of 50 ml/min over a temperature range of 15-120°C and at a scanning rate of 10°C/min. In all measurements, the DSC analyzer was calibrated using indium and an empty aluminium pan, as reference. The enthalpy of gelatinization ( $\Delta H$ ) of each sample was obtained from the peak area of the endotherm following the DSC run using the TA Universal analysis 2000 software (TA Instruments, Waters LLC, New Castle, USA). Similarly, the onset temperature ( $T_o$ ), peak temperature ( $T_p$ ) and the endset temperature of gelatinization were obtained by integration of DSC sample thermograms.

### 2.4. Diffusion/Leaching Experiments

The diffusion experiment was performed according Arroqui et al. [14] with some modifications. Deionised water was used throughout the experiments. In each experiment, a peeled potato cube (2 cm<sup>3</sup>) was heated in 500 ml deionised water at 95-98°C in a beaker, covered with aluminium foil until cooked. The cooked samples and the cooking liquid were analysed for the content of potassium using the flame atomic absorption instrumentation.

Three modes of sample pre-treatment including preheating at 80°C and 50°C as well as at varying temperatures of leaching (30-50°C) were carried out. A covered 1000 mL beaker containing 500 ml deionised water and a reservoir were placed in a thermostatically and magnetically stirred water bath (2 mag-magnetic motion, Munich, Germany) set at 1200 rpm. The temperature control was maintained within  $\pm 0.2^\circ\text{C}$ . When the temperature of the water in the beaker and the bath was at the required leaching temperature, a pre-weighed sample was lowered into the beaker and a timer started. 10 mL samples were taken at time intervals for 4 h. 14 sample pipettes were taken at each constant temperature. After each sample had been removed, 10 mL of deionised water at the same temperature from the reservoir was added to maintain a constant volume. The leached samples and the sampled liquid were all analysed for the content of potassium.

### 2.5. Statistical Analysis

Statistical analysis of data was performed using the PASW statistical programme, version 22 (SPSS Inc. IBM, Chicago, Illinois). The results reported in this work are the averages of at least three measurements. Analysis of variance (ANOVA,  $\alpha = 0.05$ ) was used to test the significance of differences between three or more treatment groups whilst an independent sample T-test ( $\alpha = 0.05$ ) was used to compare two treatment groups.

## 3. Results and Discussion

### 3.1. Moisture Content

The moisture content of samples, determined from the sample weights before and after drying, was  $82.0 \pm 1.8\%$ . A small, but significant ( $p < 0.05$ ) difference was noticed

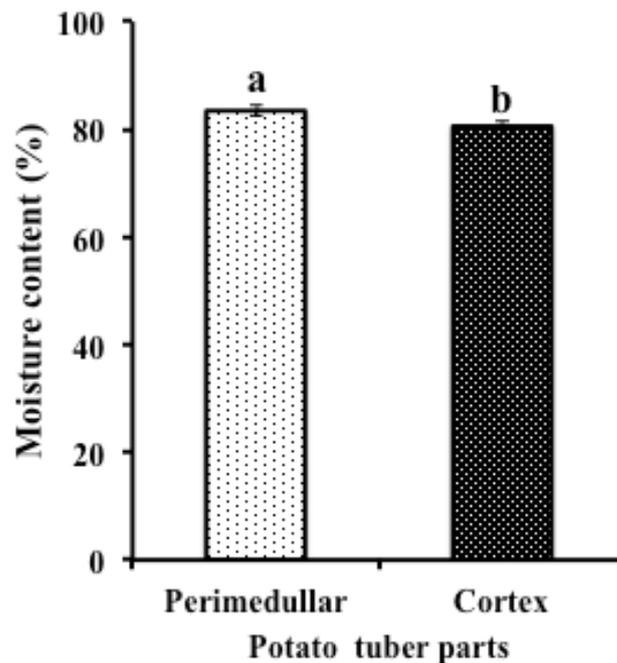
in the moisture levels of samples taken from the cortex and the perimedullary zones of the Estima potato as reported in Figure 1. The findings indicated that the cortex region of the tuber possessed more dry matter than the perimedullary area. The variation in the dry matter content between the cortex and the perimedullary was consistent within tubers and between tubers of the Estima variety. The results were not only within literature citation that the potato tuber is about 75 – 90% water but agreed with earlier findings that the water content of Bintje, King Edward and Asterix varieties decreases from the pith to storage parenchyma bud end, stem end and the cortex [22,23,24,25].

### 3.2. Scanning Electron Microscopy (SEM)

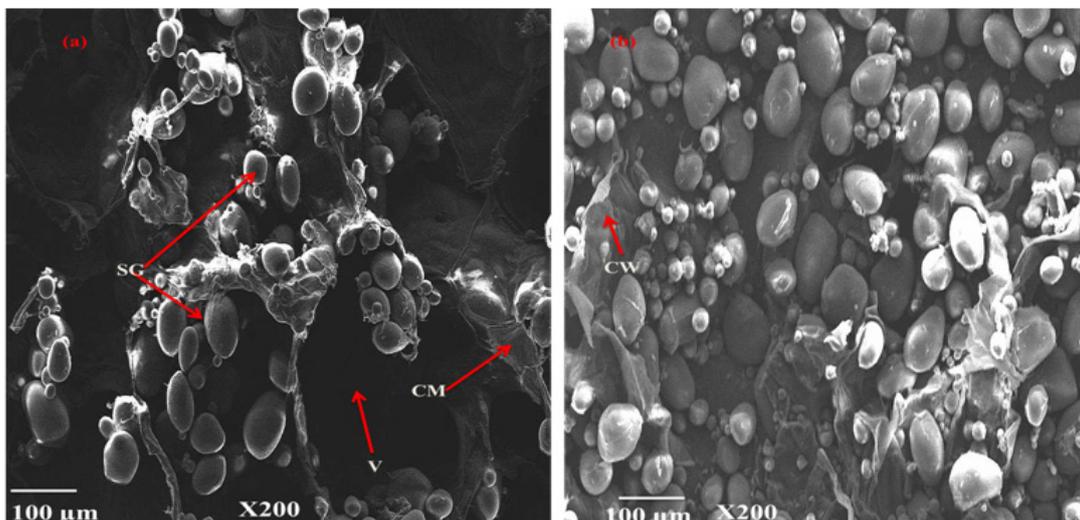
In all the analysed batches of samples, the fresh potato tissues generally appeared as a compact structure of large and small cells containing isodiametrically spherical

starch granules of different sizes. The cells were closely bonded to each other through an extensive cell-to-cell contact. The micrographs revealed apparent differences in the microstructures of samples taken from the cortex and from the perimedullary zone of the Estima potatoes as in Figure 2(a) and Figure 2(b).

It was generally observed that the samples from the cortex possessed more starch granules than those from the perimedullary region. Again, the tissues from the perimedullary region showed a very regular and more defined arrangement of cells with larger vacuoles than the cortex. The findings of more starch in the cortex than in the perimedullary zone confirm the earlier observation about the relatively higher dry matter content of the cortex. The dry matter content of potatoes is reported to be made up of about 80 % starch granules (26). The findings were also consistent with an earlier report that the cortex possessed the highest amount of starch and protein (23).



**Figure 1.** Moisture content of potato cubes from the cortex and perimedullary regions of the tuber. <sup>a-b</sup>Bars with different letters indicate significant difference at  $p < 0.05$



**Figure 2.** (a) SEM micrographs of fresh potato tissue (16°C) from the (a) perimedullary and (b) Cortex zones. CW: Cell wall, CM: Cell membrane, SG: Starch granules and V: vacuole

The nature and content of dry matter and the moisture distribution within the tuber have effects on the rate of diffusion of solutes through and out of potatoes. To the extent that moisture facilitates the diffusion rate whilst the dry matter offers resistance to the flow, differences in the content of dry matter and moisture at different regions of the potato tuber will have implications for the mechanism of potassium diffusion in fresh potatoes. The very regular and more defined arrangement of cells with larger vacuoles in the perimedullary could facilitate the free flow of moisture (with dissolved potassium). The densely packed starch granules and irregular arrangement of cells in the cortex meant that potassium in that region would have to overcome a relatively greater physiological resistance and follow a tortuous path. A more difficult flow of potassium through the cortex would therefore have implications for the rate at which potassium leaves the tissue surface into leaching water.

The effect of preheating on the microstructure of potato tissues is as illustrated in [Figure 3](#). Preheating generally affected the cell structure of potato tissues and the degree of microstructural deformation and integrity of cell walls was positively correlated with temperature. Sample preheating using the conventional microwave lasted between 10 and 30 min depending on the required preheating temperature.

From the micrographs, it was revealed that for pre-treatment temperatures up to 50°C, the cell protoplasts, which consist of the cell membrane (plasmalemma) and the cell content of the preheated tissues were intact and undamaged just like the fresh potatoes; signifying less impact. However, as the preheating temperature of tissues increased, changes in the microstructure became more visible. At 60°C, partial deformation of the cellular walls and membranes was observed along with some starch granules showing broken amyloplast membrane around their surfaces. Some partially gelatinized starch granules were also detected as shown in [Figure 3b](#).

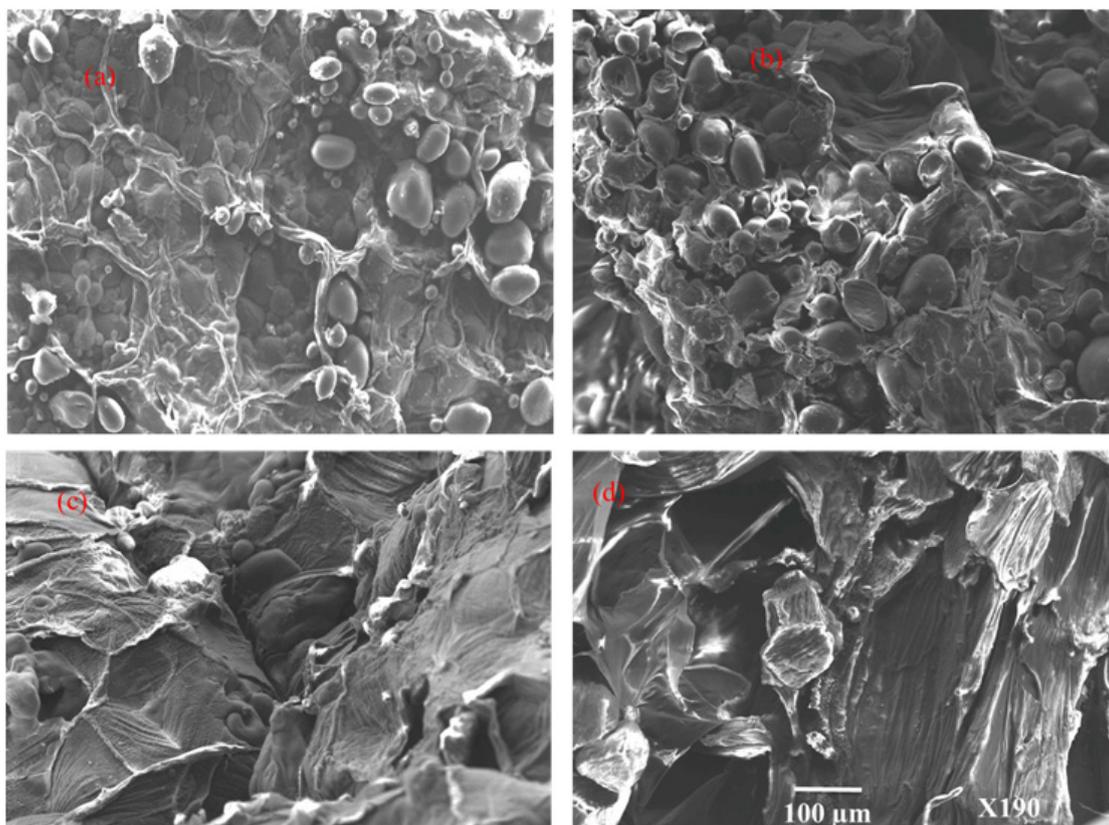
For potato tissues preheated at 75°C, the degradation of cellular wall and membrane materials was observed to be more pronounced. The enclosed cells had flatly opened up and majority of the starch granules had completely gelatinised as displayed in [Figure 3c](#). At 80°C, the potato tissues did not show any visible granule of starch. Besides the textural changes at the macroscopic level, the original outlines of the cell walls, cell membranes and the cellular cements in the matrix had been damaged. More importantly, the intercellular spaces or pores in the matrix had become enlarged or more visible and an increasing occurrence of detachments between adjacent cell walls could be noted. It is reported that textural changes resulting from the blanching and cooking of fruits and vegetables are mainly a consequence of the gellation of pectins located in the cell walls as well as their solubilisation and degradation [27]. Maximum tissue softening is reported to occur only after cellular separation [28]. The microstructural changes observed in preheated potato tissues could be attributed to the dissolution of the pectins which act as cell adhesive and the gelation of cell wall polymers culminating in cell separation with consequential effect on the diffusion matrix of potassium

through and out of potatoes. As a change in microstructure of the potato signifies a change in the physiological barrier, a reduction or removal of such resistance could enhance the rate of leaching of potassium even at lower temperature. The changing effect of heat on the microstructure of potatoes could therefore change the diffusion matrix of potassium through and out of potatoes.

### 3.3. Differential Scanning Calorimetry (DSC)

A comparison of in situ starch gelatinization properties of samples from the cortex and perimedullary tissue zones revealed considerable variations as shown in [Table 1](#). The gelatinization temperatures, especially the onset and endset, and the range within which the gelatinization process occurred were significantly higher in the perimedullary than in the cortex tissue. In addition, the average transition enthalpy was about 3 J/g lower in the perimedullary. That notwithstanding, all the parameters observed for the gelatinization of starch from the different tissue zones of Estima potato agreed with published literature [20,23,29]. The results from the study were within the commonly reported gelatinization temperature and enthalpy ranges of 57 – 80°C and 8 – 20 J/g respectively, for potato starch from other varieties [30,31].

The marked variations in the gelatinization parameters between the cortex and the perimedullary tissues were attributed to the differences in starch granules and moisture contents of the tissues. It can be explained that in excess water, the hydrogen bridges of starch are destroyed allowing water to be associated with the free hydroxyl groups, which in turn, facilitates its molecular mobility in the amorphous regions and swelling of the granules [32]. Penetration of water enhances randomness in the general starch granule structure and reduces the number of crystalline regions which do not allow water entry. The higher moisture-starch ratio of the perimedullary tissues of the Estima potatoes therefore explains its high sensitivity to starch gelatinization. Apart from the relatively higher moisture, the SEM studies showed that tissues from the perimedullary have well defined arrangement of cells containing fewer and smaller starch granules. It has been shown that isolated potato starch granules do not gelatinise simultaneously, rather, larger granules of starch tend to gelatinise granule per granule before smaller ones [33,31]. The higher gelatinization temperatures observed in the perimedullary could also be linked with the relatively smaller size of starch granules. Although no direct relationship between the dry matter content and the gelatinization parameters was observed in this study, the dry matter could have an influence on the heat transfer properties of tissues of potato. Therefore, the differences in the dry matter or moisture contents between the cortex and perimedullary tissues could plausibly explain variations in the transition enthalpies and gelatinization temperatures. Variations in transition enthalpies and gelatinization temperatures of starch from different tissue zones of the potato tuber suggest differences in microstructural changes of the different tuber zones and ultimately the diffusion matrix of soluble solutes during the leaching process.



**Figure 3.** SEM micrographs of potato tissues preheated at (a) 50°C, (b) 60°C, (c) 75°C, and (d) 80°C

**Table 1.** Gelatinization properties of starch from cortex and perimedullary tissue zones of Estima potato.

Potato sample (region)	Dry weight (mg)	Gelatinization temperature (°C)				$\Delta H$ (J/g)
		To	Tp	Te	R = Te-To	
Cortex	4.6 ± 0.3 <sup>a</sup>	64.4 ± 0.3 <sup>a</sup>	69.1 ± 0.2 <sup>a</sup>	73.0 ± 0.4 <sup>a</sup>	8.6 ± 0.1 <sup>a</sup>	17.6 ± 2.2 <sup>a</sup>
Perimedullary	3.4 ± 0.7 <sup>b</sup>	66.3 ± 0.9 <sup>b</sup>	69.9 ± 0.6 <sup>b</sup>	75.9 ± 0.2 <sup>b</sup>	9.6 ± 0.7 <sup>b</sup>	14.8 ± 0.9 <sup>b</sup>

Values are mean ± standard deviation, n = 3. <sup>a-b</sup>Values in the same column with different superscripts letters are significantly different at  $p < 0.05$ .  $\Delta H$ : Enthalpy Change. R: gelatinization temperature range.  $T_o$ ,  $T_p$  and  $T_e$  are onset temperature, peak temperature and endset temperature of gelatinization, respectively.

### 3.4. Diffusion/leaching of Potassium

Results from the cooking of raw potatoes without prior treatment pointed to a reasonable loss of potassium (44.2±1.8%) during the boiling. In the cooking of potatoes, heat is transferred from the hot water medium to the surface of the potato by natural convection boiling and from the surface to the core (inside) by conduction. As observed from the SEM micrographs, the potato matrix is composed of porous solid structures (packed with starch molecules) filled with water. As the tissue surface temperature increases towards the water boiling temperature of 100°C, heat transfer from the water at the penetrating interface along with dissolved and mobile solutes in the potatoes may be increasing. This will result in a cycle of heat and mass transfer to and through the tissue of the potatoes during the boiling thereby affecting the potassium content of the potatoes.

It was discovered that preheating, as a pre-treatment to leaching potato cubes, generally increased the ease of potassium removal. For instance, by preheating samples to

50°C and 80°C, the amount of potassium leached at each stage of sampling for leaching at 30°C, increased by about five (5) and eight (8) folds respectively as in Figure 4a. Whilst similar trends were observed for leaching at 40°C, the results for 80°C preheating were, statistically, insignificantly different from 50°C preheating for samples leached at 50°C ( $p > 0.05$ ) as shown in Figure 4b. These findings were consistent with those of the SEM and the DSC. At the sub-gelatinization temperatures, the effect of the physiological barrier (cell wall and membranes) is greater. By preheating at 80°C, such barrier would have been fully removed thereby lowering the activation energy for more potassium ions to diffuse through and out into water, even at lower leaching temperature. At or around the gelatinization temperature range, the effect of heat (from preheating or leaching water or both) is greater, enough to reduce or completely remove the physiological barrier. The reduced effect of the 80°C preheating on leaching at 50°C could therefore be linked with the increased heat-induced microstructural effect.

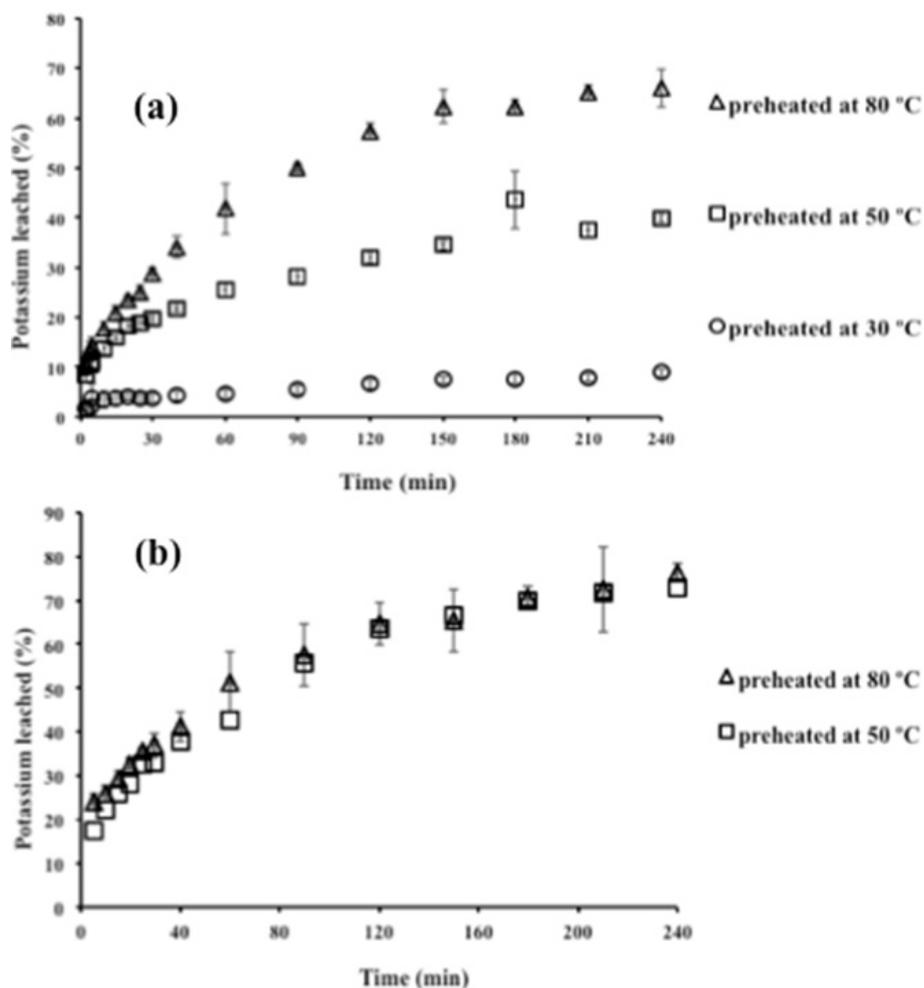


Figure 4. Potassium leached at (a) 30°C and (b) 50°C after different preheat treatments

## 4. Conclusion

The study indicated that there were significant variations in the cellular architecture, moisture content and distribution, which influenced the diffusion of potassium through and out of potatoes. The apparent microstructural variation within potato tuber also reflected in the different gelatinization properties observed for samples from different regions, including a 3 J/g higher transition enthalpy in the cortex. Preheating increased the rate of potassium diffusion out of the potato attributable to the breakdown of cellular walls and membranes with increasing temperature. As a change in microstructure signifies a change in the physiological barrier, preheating, as a technique for reducing or removing such resistance could enhance the rate of leaching of potassium even at lower temperature for renal patients.

## Conflict of Interest

The authors have declared no conflict of interest

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