



## Research Article

## Kinetic, Thermodynamic, Mass Transfer, and Determination of Controlling Steps in Pectin Extraction from Lemon Peel (*Citrus limon L. Osbeck*)

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### Abstract

Lemon peel, a byproduct of citrus processing, contains high levels of pectin valued for its functional roles in food and pharmaceutical products. This study investigates pectin extraction using a mechanistic approach based on the Shrinking Core Model (SCM), which describes the progressive reaction of solid particles. The process follows first-order kinetics, with simultaneous extraction and degradation. Optimal conditions were 95 °C, pH 1.8, and 50 minutes, yielding 36% pectin. Key parameters included extraction rate constant  $k_1 = 0.0562 \text{ min}^{-1}$ , degradation rate constant  $k_2 = 0.0039 \text{ min}^{-1}$ , activation energies  $E_{a1} = 31.7 \text{ kJ mol}^{-1}$ ,  $E_{a2} = -22.9 \text{ kJ mol}^{-1}$ , enthalpy change  $\Delta H^\circ = 76.05 \text{ kJ mol}^{-1}$ , entropy change  $\Delta S^\circ = 0.23 \text{ J mol}^{-1} \text{ K}^{-1}$ , and Gibbs free energy  $\Delta G^\circ < 0$ . The diffusion coefficient ranged from 0.055 to  $0.06 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  for 0.34 mm particles. The extraction process was controlled by both internal diffusion and chemical reactions. This study presents a novel integration of kinetic, mass transfer, and thermodynamic models, offering a predictive framework for optimizing sustainable and energy-efficient pectin production from lemon waste.

**Keywords:** Extraction, Kinetic, Mass transfer, Pectin, Shrinking core model, Thermodynamics

### 1 Introduction

Lemon (*Citrus limon L. Osbeck*) is the third most widely produced citrus fruit in the world, with an annual production of around 10.2 million tons [1]. The fruit consists of three main parts: pulp, peel, and seeds, all of which are rich in valuable components, including citric acid, ascorbic acid, flavonoids, and essential oils. Lemons are known for their bioactive compounds, including vitamins, minerals, and dietary fiber, making them highly beneficial for health [2]. In Indonesia, citrus fruits are a significant contributor to horticultural production, with production reaching 2.92 million tons in 2023, representing a 8.88% increase from the previous year [3]. Amidst the rising popularity of natural lemon juice drinks, lemon peel waste is often discarded, with some used as cattle feed.

Improper waste disposal also contributes to environmental pollution [4].

Lemon peels are a rich source of pectin, a valuable polymer with gelling and stabilizing properties, extensively used in the food and pharmaceutical industries [5]. However, the efficient recovery of pectin is challenging due to its strong association with the plant cell wall matrix, requiring controlled extraction processes to prevent structural degradation.

To optimize extraction performance and product quality, a comprehensive understanding of the kinetics governing pectin release is essential. Kinetic parameters provide insight into the extraction rate and underlying mechanism, which are strongly influenced by time, temperature, pH, and solvent conditions. Previous research has generally adopted empirical kinetic models (first- or second-order) [6], [7], while



mechanistic studies examined hydrolysis and potential degradation phenomena during extraction [8]–[10].

Mass transfer also plays a crucial role in determining the extent of pectin migration from the lemon peel matrix into the solvent phase. Studies on *Citrus aurantium* demonstrated the significance of diffusion coefficients and extraction priority in improving yield and energy efficiency [11]. These findings also highlight the importance of mass transfer analysis in optimizing extraction conditions and maximizing pectin yield.

Thermal treatment is commonly employed to enhance pectin extraction. For instance, optimal extraction from mango peels was achieved at 90 °C [9], while similar temperature ranges (70–90 °C) were optimal for cocoa peel pectin extraction [12]. Therefore, thermodynamic studies are essential for understanding temperature effects, including enthalpy, entropy, and Gibbs free energy changes during extraction.

Recent investigations have explored the kinetics, thermodynamic behavior [9], [10], mass transfer and diffusion mechanisms of pectin extraction using various plant sources [11]. Although some studies have adopted mechanistic models, they often focus on parameter estimation without identifying the dominant rate-controlling step—whether diffusion or chemical reaction. Consequently, the mechanistic understanding of the coupled extraction-degradation process remains incomplete.

To address this limitation, the present study applies the Shrinking Core Model (SCM) to describe pectin extraction from lemon peel. This model enables simultaneous evaluation of kinetic and mass transfer phenomena, allowing quantitative determination of thermodynamic parameters and identification of the rate-limiting step. The proposed approach integrates empirical and mechanistic perspectives, offering a predictive framework for optimizing sustainable citrus waste valorization and supporting industrial-scale pectin production.

## 2 Research Materials and Methods

### 2.1 Research materials

Fresh lemons (*Citrus limon L. Osbeck*) were obtained from local farmers in the Batu Malang area, Indonesia, in September 2024. The plant material was authenticated through plant identification analysis to confirm its botanical classification. Hydrochloric acid

(37%), ethanol (96% and 70%), and acetone used in this study were of analytical grade (PT. SMART LAB., Tangerang, Indonesia).

### 2.2 Pretreatment of lemon peel

The lemon underwent an initial washing process, followed by the meticulous separation of the peel from the endocarp utilizing a stainless-steel knife. Subsequently, the peel was meticulously diced into fine fragments and subjected to drying in a forced convection dryer at 60 °C until a state of constant weight was achieved. Thereafter, the sample was pulverized using an electric mill. The lemon peel powder was preserved at a temperature of 6 °C until it was required for further use.

### 2.3 Pectin extraction methods

The extraction of pectin from lemon peel was conducted in accordance with a modified method [2], [8]. In summary, desiccated lemon peels (5 g) were introduced into a specified volume of water (125 mL). The pH of the resultant mixture was carefully adjusted to 1.8 by the addition of hydrochloric acid (2 M). The mixture was subjected to thermal treatment at temperatures of 65, 75, 85, and 95 °C while being continuously agitated at a rate of 200 rpm for durations of 20, 30, 40, 50, and 60 min.

The mixture was then placed in ice to stop the extraction process. Once cooled, the supernatant was separated by filtering it through a cloth.

To induce coagulation, an equal volume of 96% ethanol was added to the filtrate, which was then left undisturbed at room temperature for 20 h. The formed precipitate was collected using vacuum filtration with a porcelain funnel lined with filter paper. It was first washed with 70% acidic ethanol containing 0.5% HCl, followed by 70% ethanol, and finally with 96% ethanol. Three washes with acetone further purified the extracted pectin, and then it was dried in an oven at 60 °C until a constant weight was reached.

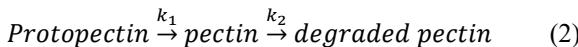
The yield of pectin extracted from lemon peel was determined using Equation (1)

$$YPe (\%) = \frac{mPe}{mLP} \times 100 \quad (1)$$

where  $YPe$  represents the percentage (%) of extracted pectin,  $mPe$  denotes the mass of the obtained pectin in grams (g), and  $mLP$  refers to the initial weight of the lemon peel powder.

## 2.4 Kinetics of pectin extraction

Pectin extraction involves two simultaneous transformations: the diffusion of pectin from the matrix to the solvent and the partial degradation of the dissolved pectin. A mathematical model, based on the assumption of simultaneous hydrolysis and degradation reactions, was derived from the Pancev model using the first-order approach [13]. The reaction scheme can be represented as follows:



The kinetic equation is derived as follows.

$$r P_o(t) = \frac{dP_o(t)}{dt} = -k_1 P_o(t) \quad (3)$$

$$r P_e(t) = \frac{dP_e(t)}{dt} = k_1 P_o(t) - k_2 P_e(t) \quad (4)$$

Where  $r_{P_o}(t)$  and  $r_{P_e}(t)$  are the rates of change of protopectin and extracted pectin, respectively ( $\text{mg g}^{-1} \text{ min}^{-1}$ ).  $k_1$  and  $k_2$  are the rate constants for pectin extraction and degradation ( $\text{min}^{-1}$ ), and  $t$  is the extraction time (min).  $P_o(t)$ ,  $P_e(t)$ , and  $P_d(t)$  represent the amounts of protopectin remaining in the lemon peel matrix, pectin extracted into the solvent, and degraded pectin at the time  $t$ , respectively ( $\text{mg g}^{-1}$  of dry lemon peel).

The concentration of protopectin,  $P_o(t)$ , can be obtained by integrating Equation (3):

$$\int_{A_o}^{P_o} \frac{dP_o(t)}{P_o(t)} = -k_1 dt \quad (5)$$

$A_o$  is the total protopectin in the matrix, pectin extracted, and degraded pectin.

$$A_o = P_o(t) + P_e(t) + P_d(t) \quad (6)$$

where  $A_o$  is the initial total amount of pectin-related components ( $\text{mg g}^{-1}$  of dry lemon peel).

By solving Equation (5), we obtain (Equation (7)):

$$\ln \frac{P_o(t)}{A_o} = -k_1 t \quad (7)$$

$$P_o(t) = A_o e^{-k_1 t} \quad (8)$$

To obtain  $P_e(t)$ , Substituting Equation (8) into Equation (4) gives:

$$P_e(t) = \frac{k_1 A_o}{(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t}) \quad (9)$$

The degraded pectin,  $P_d(t)$ , is obtained by substituting Equations (8) and (9) into Equation (6):

$$A_o = A_o e^{-k_1 t} + \frac{k_1 A_o}{(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t}) + P_d \quad (10)$$

$$P_d(t) = A_o (1 + \frac{k_2}{(k_1 - k_2)} e^{-k_1 t} + \frac{k_1}{(k_2 - k_1)} e^{-k_2 t}) \quad (11)$$

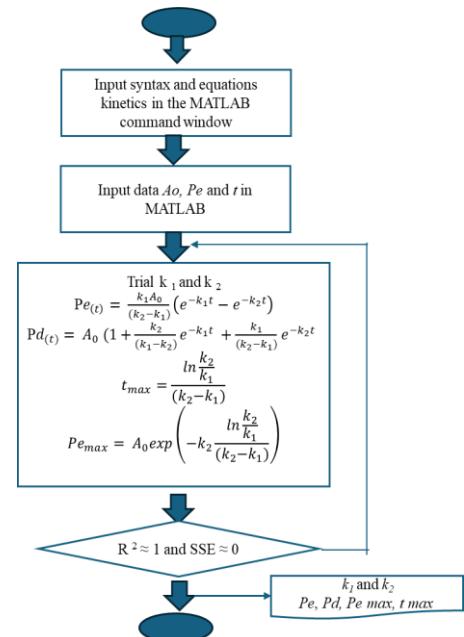
The extraction time corresponding to the maximum amount of extracted pectin ( $P_{e,\max}$ ) is defined as  $t_{\max}$ . It can be determined by setting the first derivative of Equation (9) to zero, yielding:

$$t_{\max} = \frac{\ln \frac{k_2}{k_1}}{(k_2 - k_1)} \quad (12)$$

Equation (12) substituted into equation (9) gives the maximum extracted pectin:

$$P_{e,\max} = A_o \exp \left( -k_2 \frac{\ln \frac{k_2}{k_1}}{(k_2 - k_1)} \right) \quad (13)$$

Experimental data of pectin yield ( $P_e$ ) and extraction time ( $t$ ) were fitted using MATLAB R2024a until  $R^2$  approached 1 and RMSE approached 0. The parameters  $P_e$ ,  $P_d$ ,  $P_{e,\max}$ , and  $t_{\max}$  were then calculated as illustrated in Figure 1.



**Figure 1:** Workflow for determining the kinetic parameters of the simultaneous extraction-degradation model using MATLAB.



## 2.5 Determination of total protopectin ( $A_o$ ) methods

The initial protopectin content ( $A_o$ ) in lemon peel was determined through a multistage acid extraction carried out under the optimal conditions predicted by MATLAB (pH 1.8, 95 °C, and 50 min), following the extraction procedure described in Section 2.3 and the method previously reported by [13]. Dilute hydrochloric acid was used as the extraction solvent. After each extraction stage, the solid residue was filtered and subjected to further extraction under identical conditions until no additional pectin could be recovered from the peel matrix, indicating complete depletion of protopectin. The cumulative amount of pectin obtained from all stages was considered as the initial protopectin content ( $A_o$ ). The average value of  $A_o$  determined from three independent extractions was  $44.30 \pm 0.12 \%$ , representing the total protopectin present in the raw lemon peel under the specified extraction conditions.

## 2.6 Thermodynamics of pectin extraction

The Arrhenius Equation (14) and the values of kinetic constants ( $k_1$  and  $k_2$ ) were used to calculate the activation energies ( $Ea$ ) at various temperatures. Utilizing the values,  $Ea$  was computed. The slope of the graph of  $\ln k$  vs.  $1/T$  is equal to  $-Ea/R$  as follows:

$$k = Ae^{-Ea/RT} \quad (14)$$

$$\ln k = \ln A - \frac{Ea}{RT} \quad (15)$$

where  $k$  is the rate constant ( $\text{min}^{-1}$ ),  $A$  is the pre-exponential factor,  $Ea$  is the activation energy ( $\text{J mol}^{-1}$ ),  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is the absolute temperature (K).

The thermodynamic activation parameters, namely the enthalpy ( $\Delta H^\ddagger$ ) and entropy ( $\Delta S^\ddagger$ ) of activation, were determined using the Eyring equation (Equation (16)) based on transition state theory [8], [14]:

$$k = \left( \frac{K_B T}{h} \right) e^{\frac{\Delta S^\ddagger}{R}} \cdot e^{-\left( \frac{\Delta H^\ddagger}{RT} \right)} \quad (16)$$

$$\ln \left( \frac{k}{T} \right) = \ln \left( \frac{K_B}{h} \right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{R} \left( \frac{1}{T} \right) \quad (17)$$

In this equation,  $k$  is the rate constant ( $\text{min}^{-1}$ ),  $T$  is the absolute temperature (K),  $K_B$  is the Boltzmann constant ( $1.381 \times 10^{-23} \text{ J K}^{-1}$ ),  $h$  is the Planck constant ( $6.626 \times 10^{-34} \text{ J s}$ ),  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1}$

$\text{K}^{-1}$ ),  $\Delta H^\ddagger$  is the activation enthalpy ( $\text{J mol}^{-1}$ ), and  $\Delta S^\ddagger$  is the activation entropy ( $\text{J mol}^{-1} \text{ K}^{-1}$ ). The slope of the linear plot of  $\ln(k/T)$  versus  $1/T$  corresponds to  $-\Delta H^\ddagger/R$ , and the intercept represents:

$$\text{intercept} = \ln \left( \frac{k_B}{h} \right) + \frac{\Delta S^\ddagger}{R} \quad (18)$$

Estimation of the magnitudes of  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  in pectin extraction using the van't Hoff equation at equilibrium conditions [9], [11], [15]:

$$\ln K = \left( \frac{-\Delta H^\circ}{R} \right) \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (19)$$

Here,  $K$  is the equilibrium constant, defined as the ratio between the maximum extracted pectin and the remaining protopectin at the corresponding time ( $K = P_{e \max} / P_o(t_{\max})$ ). The slope of the plot of  $\ln K$  versus  $1/T$  gives  $-\Delta H^\circ/R$ , while the intercept gives  $\Delta S^\circ/R$ . The standard Gibbs free energy change ( $\Delta G^\circ$ ) was calculated from:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (20)$$

## 2.7 Mass transfer of pectin extraction

Mass transfer during pectin extraction can be described by Fick's second law of diffusion, which governs the molecular transport of solutes [11]. In this context, diffusivity ( $D$ ) plays a crucial role in determining the rate of mass transfer and is essential for designing industrial equipment.

In batch extraction processes, mass transfer occurs through two main diffusion mechanisms: internal and external diffusion. Internal diffusion of active compounds, as outlined in Fick's law, is driven by the concentration gradient between the plant matrix and the surrounding solvent. Several basic assumptions used to simplify the mass transfer problem in pectin extraction [13] are as follows:

- 1) The solid particles form a matrix in which protopectin is evenly distributed.
- 2) Insoluble protopectin is converted to pectin through acid hydrolysis in the solid phase.
- 3) The solid particles are spherical in shape.
- 4) Particle geometry remains unchanged during solvent penetration.
- 5) The mass transfer of pectin from solid particles occurs via diffusion, with a diffusion coefficient assumed to be constant over time.
- 6) External mass-transfer resistance is assumed to be negligible. The applied constant agitation (200

rpm) reduces external film resistance, and subsequent experimental analysis confirms that external mass transfer contributes minimally to the overall mass transfer rate.

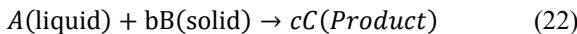
To determine the effective diffusivity coefficient ( $D_e$ ), the equilibrium amount of solute ( $P_{e,\max}$ ) was used in the following Equation (21) [11]:

$$\ln \frac{P_{e,\max}}{P_{e,\max} - P_e} = \ln A + \frac{\pi^2 D_e t}{R^2} \quad (21)$$

where  $P_e(t)$  is the amount of pectin extracted at time  $t$  (g solute/g solid),  $P_{e,\max}$  is the amount of pectin at equilibrium (g solute/g solid),  $D_e$  is the effective diffusion coefficient ( $\text{m}^2/\text{s}$ ), and  $R$  is the average particle radius (m). The average particle size of the lemon peel powder was 0.34 mm (30–40 mesh), corresponding to a radius of  $1.7 \times 10^{-4}$  m.

## 2.8 Determination of controlling steps of pectin extraction

Heterogeneous reactions between solids and liquids, reacting and then transforming into products, are represented as follows (Equation (22)) [15]:



In this system,  $A$  represents the solvent,  $B$  denotes protopectin in the solid matrix, and  $C$  corresponds to the pectin formed in both the solid and liquid phases.

Based on the first-order kinetic approach, the reaction conversion that occurs is as follows (Equation (23)) [16]:

$$X = \frac{N_{B0} - N_B}{N_{B0}} \quad (23)$$

Where  $N_{B0}$  is the number of moles of  $B$  (protopectin) in the particle at the beginning of leaching,  $N_B$  is the number of moles of  $B$  at time  $t$ .

During the reaction, the size of solid particles remains unchanged if the products are formed according to the reaction mechanism. This phenomenon is described as the Shrinking Core Model (SCM) Constant Particle Size. The SCM describes three sequential stages [16], [17]:

1) External diffusion, where  $A$  diffuses through the liquid film surrounding the solid particle

2) Internal diffusion, where  $A$  penetrates the product layer to reach the unreacted core

3) Chemical reaction, where  $A$  reacts with the solid  $B$  at the interface.

Each step can be expressed mathematically as follows (Equations (24)–(26)):

- External diffusion control:

$$\frac{t}{\tau} = 1 - \left(\frac{r_c}{R}\right)^3 = X_B \quad (24)$$

- Internal diffusion control:

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{\frac{2}{3}} + 2(1 - X_B) \quad (25)$$

- Chemical reaction control

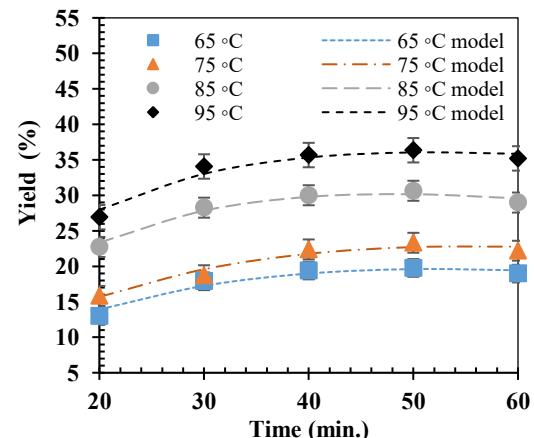
$$\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3} \quad (26)$$

Where  $X_B$  is the fractional conversion of the solid reactant,  $r_c$  is the radius of the unreacted core at time  $t$ ,  $R$  is the initial particle radius, and  $\tau$  is the characteristic time required for complete conversion under the respective controlling mechanism

## 3 Results and Discussion

### 3.1 Kinetics of lemon peel pectin extraction analysis

The kinetic behavior of pectin extraction from lemon peel was described using a first-order model that incorporates simultaneous reactions (Figure 2). The model fitted the experimental data well, with a determination coefficient ( $R^2$ ) exceeding 0.94 and RMSE & SSE near zero (Table 1), confirming the validity of the model. These results support the assumption of concurrent reaction proposed in Equation (2) involving protopectin hydrolysis ( $k_1$ ) and pectin degradation ( $k_2$ ).



**Figure 2:** Experimental and modelled pectin yield  $P_{e(t)}$  versus time at different temperatures.



As shown in Table 1, the value of  $k_1$  is consistently higher than  $k_2$ , and the  $k_2$  value gradually decreases within the temperature range of 75–95 °C. Although elevated temperatures generally promote depolymerization, the observed decline in  $k_2$  suggests a competing mechanism between extraction and degradation kinetics. Implying that extraction predominates over degradation at shorter contact times [9].

A similar trend was reported by previous studies in pectin extraction from mango and pineapple peel [9], [18]. Zhang *et. al.*, [19] also found that extraction of pectin from apple pomace at temperatures up to 120 °C was governed by a balance between strong extraction ability and mild degradation, indicating that moderate thermal intensification enhanced yield without significant depolymerization. This interpretation is consistent with the activation energy results presented later (Table 2), confirming that degradation can still occur under these conditions. However, its contribution to the overall process becomes less as the temperature increases.

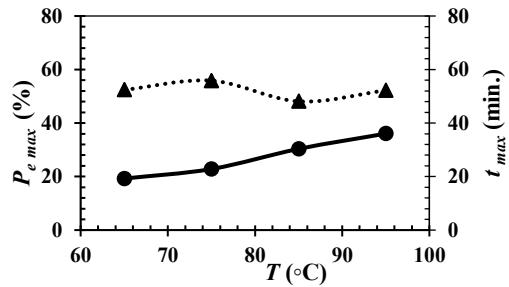
**Table 1:** Kinetic rate constants for pectin extraction at different temperatures.

$T$ (°C)	$k_1$ (min <sup>-1</sup> )	$k_2$ (min <sup>-1</sup> )	Correlation Coefficient
65	0.0231	0.0155	$R^2 = 0.9449$ RMSE = 0.0058 SSE = 0.000170
75	0.0257	0.0119	$R^2 = 0.9535$ RMSE = 0.0060 SSE = 0.000183
85	0.043	0.008	$R^2 = 0.9535$ RMSE = 0.0060 SSE = 0.000183
95	0.0541	0.0039	$R^2 = 0.9699$ RMSE = 0.0049 SSE = 0.000120

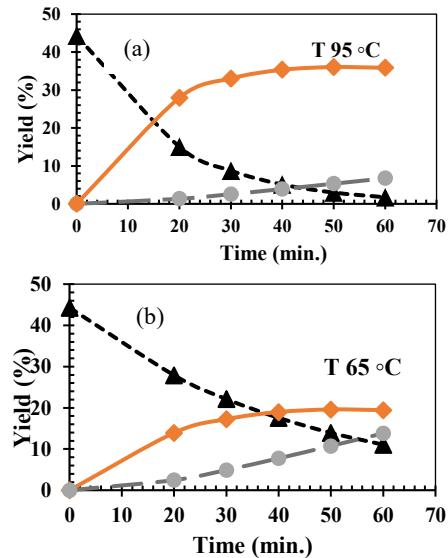
Figure 3 illustrates the relationship between pectin yield ( $P_{e\max}$ ) and extraction time ( $t_{\max}$ ) at different temperatures were determined using Equation (13), demonstrating the predictive capability of the kinetic model. The highest yield (36%) was obtained at pH 1.8 and 95 °C for 50 min. These results align with earlier research, which also reported that higher temperatures combined with shorter extraction times, favor pectin recovery. For instance, pectin extraction from mango peel produced high yield and quality at 90 °C, pH 1.5, and 120 min, showing its potential for food and pharmaceutical applications [20]. Similarly, extraction from cassava root cortex achieved an optimal yield of 71.83% under acidic conditions at 70 °C for 60 min [21], while pectin from

*Citrus sinensis* peel yielded 23.64% at 95 °C, pH 1.5, and 90 min [22].

The estimated yields of protopectin, extracted pectin, and degraded pectin obtained from the mechanistic kinetic model are shown in Figure 4(a) and (b). The residual protopectin  $P_o(t)$  and degraded pectin  $P_d(t)$  were calculated using Equation (10) and Equation (11), respectively, confirming the concurrent nature of protopectin hydrolysis and pectin degradation throughout the extraction process at 65°C, pectin extraction remains incomplete, and degradation occurs simultaneously, whereas at 95 °C, extraction proceeds rapidly to reach its maximum yield with slight degradation. These kinetic profiles highlight the strong influence of temperature on both the reaction rate and product stability, forming a solid foundation for the thermodynamic analysis that follows.



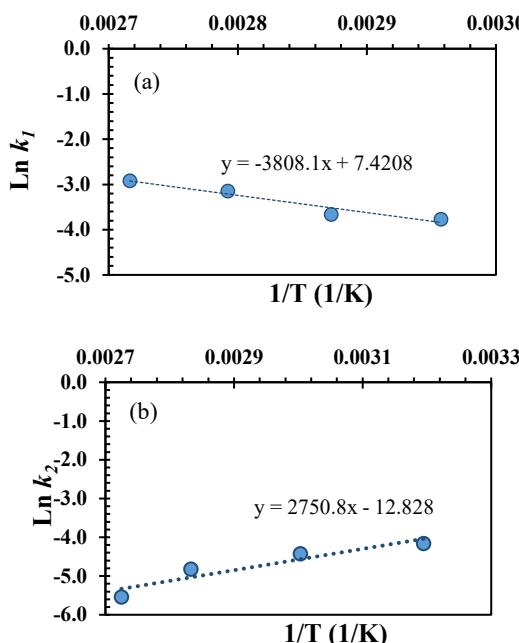
**Figure 3:** Prediction of maximum pectin extraction yield,  $P_{e\max}$  [■] versus time,  $t_{\max}$  [▲] at different temperatures.



**Figure 4:** Predicted yield of protopectin  $P_o(t)$  [■], extracted pectin  $P_e(t)$  [●], degraded pectin  $P_d(t)$  [●] at (a) 95 °C and (b) 65 °C.

### 3.2 Thermodynamics of lemon peel's pectin extraction analysis

The effect of temperature on the rate of hydrolysis, diffusion, and degradation is described using the Arrhenius equation. Figure 5(a) and (b) show the plot of  $\ln k_1$  and  $\ln k_2$  versus  $1/T$ . As the temperature increases,  $\ln k_1$  rises while  $\ln k_2$  decreases, indicating that higher extraction temperatures enhance the hydrolysis and diffusion of protopectin but suppress the apparent degradation rate. The linear trends observed in the Arrhenius plots follow Equation (15), where the slope corresponds to  $-E_a/R$ , confirming the temperature dependence of both reactions.



**Figure 5.** Arrhenius plots of (a)  $\ln k_1$  and (b)  $\ln k_2$  versus  $1/T$  for pectin extraction and degradation.

The activation energy ( $E_a$ ) of pectin extraction represents the minimum energy required for the

hydrolysis of protopectin into pectin, the diffusion of pectin, and the degradation that occurs at varying extraction temperatures. In addition,  $E_a$  also shows the energy layer of pectin in the lemon fruit matrix that needs to be overcome for hydrolysis and diffusion into the solvent ( $E_{a1}$ ) and the energy that causes pectin to begin degrading ( $E_{a2}$ ). The values of  $E_{a1}$  and  $E_{a2}$  in the extraction of pectin from lemon peel are presented in Table 2

The positive activation energy for extraction ( $E_{a1} = 31.70 \text{ kJ mol}^{-1}$ ) confirms that higher temperatures facilitate protopectin solubilization. Conversely, the negative value for degradation ( $E_{a2} = -22.90 \text{ kJ mol}^{-1}$ ) implies that degradation is spontaneous but becomes less dominant at higher temperatures. This observation is consistent with previous reports on mango peel pectin ( $E_{a1} = 5.53 \text{ kJ mol}^{-1}$ ,  $E_{a2} = -29.13 \text{ kJ mol}^{-1}$  [8]), indicating that pectin cannot be extracted entirely without minor degradation.

**Table 2:** Activation energy on the kinetics of pectin extraction from lemon peel.

T°C	T (K)	$k_1$ (min <sup>-1</sup> )	$k_2$ (min <sup>-1</sup> )	$E_{a1}$ (kJ/mol)	$E_{a2}$ (kJ/mol)
65	338	0.0231	0.0155	31.70	-22.90
75	348	0.0257	0.0119		
85	358	0.0430	0.0080		
95	368	0.0541	0.0039		

Thermodynamic parameters such as enthalpy ( $\Delta H^\ddagger$ ), entropy ( $\Delta S^\ddagger$ ), and Gibbs free energy ( $\Delta G^\ddagger$ ) were evaluated using the Eyring equation, while equilibrium-based parameters ( $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$ ) were obtained from the Van't Hoff relationship. The results are summarized in Table 3. The enthalpy and entropy of activation ( $\Delta H_\ddagger^\ddagger$  and  $\Delta S_\ddagger^\ddagger$ ) were determined using Equation (17) and Equation (18), where the slope and intercept of the Eyring plots correspond to  $\Delta H_\ddagger^\ddagger/R$  and  $\Delta S_\ddagger^\ddagger/R$ , respectively. The equilibrium parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  were evaluated using Equation (19), while the Gibbs free energy change ( $\Delta G^\circ$ ) at each temperature was calculated using Equation (20).

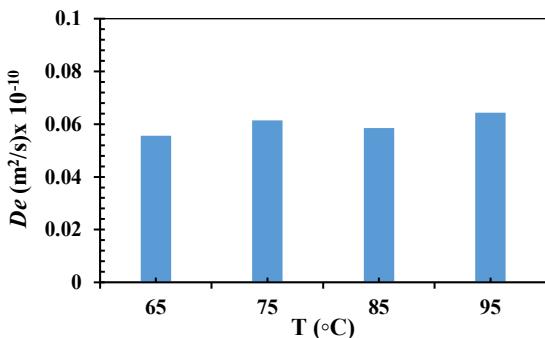
**Table 3:** Thermodynamic parameters of pectin extraction from lemon peel.

T°C	$\Delta H^\ddagger$ (kJ/mol)		$S^\ddagger$ (kJ/mol.K)		$\Delta G^\ddagger$ (kJ/Mol)		$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol.K)	$\Delta G^\circ$ (kJ/mol)
	$\Delta H_\ddagger^\ddagger$	$\Delta H_\ddagger^\ddagger$	$\Delta S_\ddagger^\ddagger$	$\Delta S_\ddagger^\ddagger$	$\Delta G_\ddagger^\ddagger$	$\Delta G_\ddagger^\ddagger$			
65	28.73	-49.60	-0.19	-0.43	93.97	94.57	76.05	0.23	-0.69
75					95.90	98.83			-2.96
85					97.83	103.10			-5.23
95					99.75	107.36			-7.50



### 3.3 Mass transfer of lemon peel's pectin extraction analysis

The relationship between the diffusion coefficient and temperature is presented in Figure 6. The calculated  $D_e$  values ranged from  $0.555$  to  $0.060 \times 10^{-10} \text{ m}^2/\text{s}$ , showing no significant variation across the temperature range of  $65\text{--}95^\circ\text{C}$ . This indicates that external mass transfer resistance was effectively minimized by reducing the lemon peel particle size to  $30\text{--}40$  mesh ( $\approx 0.34 \text{ mm}$ ) and maintaining a constant agitation rate of  $200 \text{ rpm}$ . Under these conditions, the concentration boundary layer surrounding the solid particles becomes sufficiently thin, allowing the overall process to be governed primarily by internal diffusion and chemical reaction mechanisms.



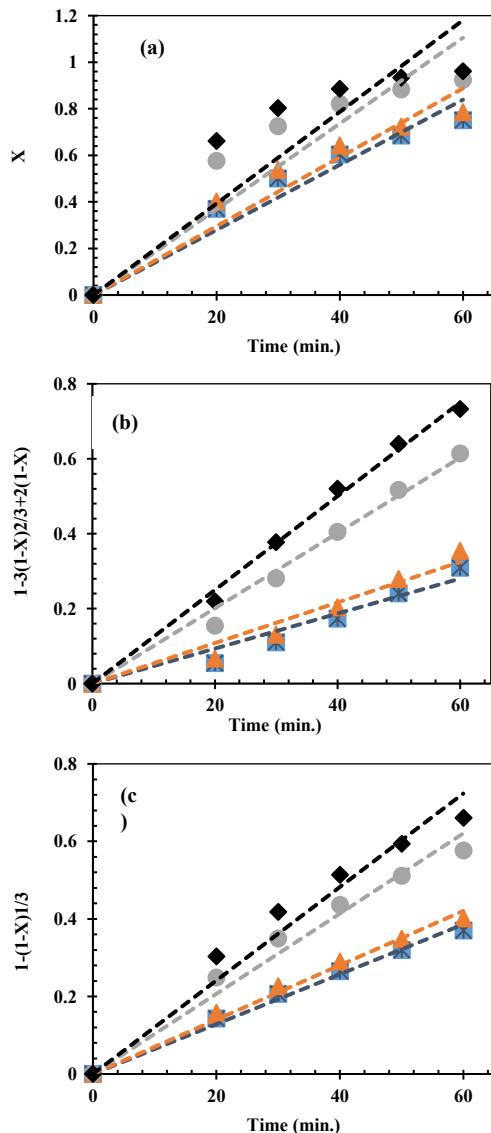
**Figure 6:** Diffusion coefficient of pectin extraction at different temperatures.

These values are lower than those reported for the extraction of pectin and hesperidin from FAI powder ( $0.425 \text{ mm}$ ), where diffusion coefficients of  $2.26\text{--}3.10 \times 10^{-10} \text{ m}^2/\text{s}$  were observed at  $313\text{--}333\text{K}$  [11]. This result suggests that the dense lemon peel matrix imposes higher internal mass-transfer resistance, confirming that internal diffusion remains the dominant limiting step in the extraction process.

### 3.4 Determination of controlling steps of pectin extraction

The extraction of solid components into a liquid phase may be governed by several mechanisms, including external diffusion through the liquid film, internal diffusion within the solid matrix, or chemical reaction at the solid-liquid interface. To determine the dominant rate-controlling step, three kinetic models were evaluated under each mechanism (Figure 7).

The conversion of protopectin to soluble pectin was analyzed by plotting each controlling model against extraction time. The mechanism showing the most linear relationship (highest  $R^2$ ) indicates the rate-determining step. As suggested by Faraji [16], fitted lines must pass through the origin to ensure zero conversion at time zero; otherwise, model accuracy is compromised.



**Figure 7:** Modelling of rate determination step in pectin extraction: (a) external diffusion control, (b) internal diffusion control, (c) chemical reaction controls at different temperatures ( $\diamond 95^\circ\text{C}$ ,  $\circ 85^\circ\text{C}$ ,  $\blacksquare 75^\circ\text{C}$ ,  $\blacktriangle 65^\circ\text{C}$ ).

The comparison of  $R^2$  values at different temperatures (Table 4) shows that the chemical reaction model provided the best fit (average  $R^2 = 0.9952$ ) at lower temperatures (65–75 °C), whereas internal diffusion became more dominant at higher temperatures (85–95 °C). This shift reflects the temperature dependence of both phenomena: the chemical reaction rate increases exponentially with temperature according to the Arrhenius law, while the internal diffusion coefficient increases more gradually, as described by Fick's law [11], [23]. Therefore, at elevated temperatures, diffusion resistance becomes relatively more significant, resulting in a mixed control mechanism where both reaction and diffusion contribute to the overall rate.

**Table 4:** Correlation coefficients ( $R^2$ ) for different rate-controlling mechanisms.

T (°C)	R <sup>2</sup> of each Mechanism Control		
	External Diffusion	Internal Diffusion	Chemical Reaction
65	0.9861	0.9828	0.9981
75	0.9834	0.9855	0.9977
85	0.9639	0.9969	0.994
95	0.9516	0.9987	0.9909
Avg	0.9713	0.9910	0.9952

These results are also supported by activation energy data ( $E_a$ ). Activation energy can serve as a key parameter in identifying the rate-controlling step of the extraction process. If the activation energy exceeds 40 kJ/mol, the process is controlled by chemical reactions. Conversely, if it is below 20 kJ/mol, diffusion dominates. When the activation energy falls between these values, both diffusion and chemical reactions contribute to the extraction process [16]. In this study, the apparent activation energy of 31.7 kJ mol<sup>-1</sup> falls within the mixed-control region, confirming that both internal diffusion and chemical reaction jointly govern the extraction process. The effective diffusion coefficient ( $D_e$ ) for lemon peel pectin extraction, ranging from  $0.055\text{--}0.060 \times 10^{-10}$  m<sup>2</sup>/s for 0.34 mm particles, further supports this conclusion.

#### 4 Conclusions

This study established a comprehensive kinetic and thermodynamic framework for pectin extraction from lemon peel under acidic conditions. The first-order mechanistic model accurately described the concurrent protopectin hydrolysis and degradation

reactions, showing strong agreement with experimental data ( $R^2 > 0.94$ ). The extraction rate constant ( $k_1$ ) increased with temperature, while the degradation rate constant ( $k_2$ ) decreased, indicating that extraction predominates at shorter contact times. Thermodynamic analysis confirmed that the process is endothermic and spontaneous ( $E_a = 31.7$  kJ mol<sup>-1</sup>;  $D_e = 0.055\text{--}0.060 \times 10^{-10}$  m<sup>2</sup>/s), governed by a mixed control mechanism involving both internal diffusion and chemical reaction.

The identification of this dual control has direct implications for process design and optimization. Since both reaction kinetics and mass transfer influence pectin yield, operational parameters such as pH, temperature, agitation rate, and particle size must be carefully balanced to minimize diffusion resistance while maintaining favourable reaction rates. This understanding provides a quantitative foundation for scaling up lemon peel pectin extraction and improving energy efficiency in intensified systems such as ultrasound- or microwave-assisted reactors, thereby supporting sustainable valorisation of citrus-processing by-products.

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#### Author Contributions

V.N.: conceptualization, methodology, investigation, data curation, formal analysis, and writing—original draft; L.A.H.: supervision, validation, methodological guidance, and writing—review and editing; I.D.G.A.P.: supervision, resources, data interpretation, and writing—review and editing; T.S.: project administration, conceptualization, supervision, funding acquisition, and writing—review and editing. All authors have read and approved the final version of the manuscript.

#### Conflicts of Interest

The authors declare no conflict of interest.



## Declaration of generative AI and AI-assisted technologies in the writing process

The authors used the ChatGPT tool to enhance the clarity and readability of the manuscript. All interpretations, analyses, and conclusions are solely the responsibility of the authors.

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