

Kinetics and model building of leaching of water-soluble compounds of *Tilia* sapwood

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Abstract

The kinetics of the leaching of water-soluble compounds of *Tilia* sapwood was investigated. A batch leaching model, based on the assumption of a second-order mechanism for the leaching, was developed to predict the rate constant of leaching, the saturated leaching capacity, and the initial leaching rate with various leaching temperatures. The rate constant is a function of the temperature, and the leaching of water-soluble compounds of *Tilia* sapwood is an endothermic process. In addition, the activation energy of leaching was also determined based on the second-order rate constants of the leaching.

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1. Introduction

The *Tilia* sapwood, contains many molecules in particular sugars, lipids, catechic and gallic tannins, polyphenolic compounds, organic acids, mineral salts, amino acids, vitamins, and essential oils [1]. *Tilia* has been known for its pharmacological properties and is used in medicines [2–5]. The molecules involved in these activities are present in the flowers and sapwood [6]. These compounds are obtained by a succession of operations, which always begins with a solid–liquid leaching with the accurate solvent [7]. Many attempts have been made to formulate a general expression describing the kinetics of leaching systems [8].

The rate of leaching is the most important parameter when batch leaching systems have to be designed. Consequently, it is of prime importance to establish the time dependence of such systems under various process conditions. Numerous

leaching processes have been studied in an attempt to find a suitable explanation for the mechanism and kinetics of the leaching processes. Leaching of xylan from hardwood species were modeled as the sum of two parallel first-order reactions, one fast and one slow [9]. The parallel first-order reaction model for the leaching of lignin from white fir sapwood with supercritical *tert*-butyl alcohol was also presented [10]. Furthermore, a kinetic model for wood leaching processes with organic solvents was reported based on the three steps of: (a) solubilization of rosin at easily accessible surface sites, (b) solubilization of less-accessible sites following diffusion of the solute into the wood pores, and (c) solubilization of intracellular rosin accessed via osmosis or the rupture of cell membranes [11].

In this study, the mechanism of leaching of water-soluble compounds of *Tilia* sapwood and kinetics was investigated in a batch reactor. A method is presented for determining the activation energy of leaching and the initial leaching rate based on a second-order leaching process. Rate parameters were defined and are used to describe the phenomenon and to predict the weight of aqueous leached dry matter of *Tilia* sapwood.

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2. Materials and methods

The leaching was carried out in a batch double-jacketed reactor of a 2 L volume equipped with a variable-speed mechanical stirrer and a thermal probe. The working part of the stirrer is blade-shaped. The temperature of the medium was maintained at a constant level by circulation of a thermal fluid (glycoled water) in the double-jacket of the reactor. Seven hundred millilitres of deionized water was initially introduced into the reactor and then heated to the study temperature. An amount of the particles was added to have the solid/water ratio 0.14, then introduced into the medium, and the mixture was stirred at this temperature during the study period. The experimental set-up of the process is shown in Fig. 1.

The influence of temperature on the leaching kinetics was studied while keeping all other factors constant. Therefore, these experiments were carried out a particle size of 0.286–0.348 mm, and a stirring speed of 100 rpm at 313, 323, 333, 353, and 363 K. The goal of this operation was to evaluate the enrichment of dry matter in the extract, since it was shown in a previous work [12] that the concentration of target molecules (reducing sugars) is a linear function of the concentration of the water-soluble material. The kinetics of leaching was evaluated by withdrawing samples of 50 ml from the leaching medium at various times. After filtering off the solids, the extracts were dried in an oven heated to 80 °C until a constant weight was obtained. The amount of dry matter obtained was then calculated.

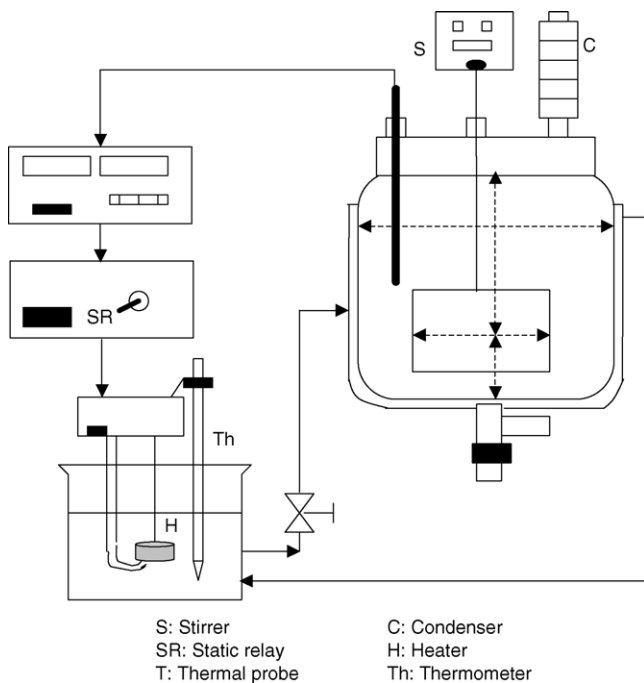
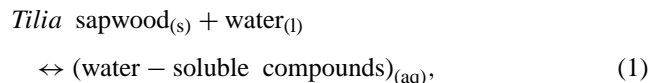


Fig. 1. Experimental set-up of the process.

2.1. Kinetic model

Temperature significantly affects the concentration of leached sapwood; leaching must be a principal concern in the overall process, as in the case of the leaching of water-soluble compounds from *Tilia* sapwood [9,13]. The leaching was simply assumed to proceed as:



assuming that the operation is only a function of the water-soluble compounds in suspension because the activities of the solid (*Tilia* sapwood) and the pure liquid (water) are unity. The concentration of level of saturated water-soluble compounds in suspension is considered constant for the same leaching conditions. After the water-soluble compounds have dissolved into suspension, the derivatives diffuse from the porous *Tilia* sapwood particles into the bulk liquid phase.

The leaching order and rate constant must be determined by experiments. Therefore, a second-order rate law expression for the leaching, which demonstrates how the rate depends on the water-soluble compounds dissolved to suspension, was described. The second-order kinetic rate equation can be written as follows:

$$\frac{dC_t}{dt} = k(C_s - C_t)^2, \quad (2)$$

where k is the second-order leaching rate constant ($L g^{-1} \text{min}^{-1}$), C_s the leaching capacity which is the concentration of water-soluble compounds at saturation ($g L^{-1}$), and C_t is the concentration of water-soluble compounds of *Tilia* sapwood in the suspension at any time, t (min).

The integrated rate law for a second-order leaching by the boundary conditions $t=0$ to t and $C_t=0$ to C_t , was obtained Eq. (3) and a linear form Eq. (4).

$$C_t = \frac{C_s^2 kt}{1 + C_s kt} \quad (3)$$

$$\frac{t}{C_t} = \frac{1}{kC_s^2} + \frac{t}{C_s}. \quad (4)$$

The leaching rate can be obtained from Eq. (4) as:

$$\frac{C_t}{t} = \frac{1}{(1/kC_s^2) + (t/C_s)}. \quad (5)$$

The initial leaching rate, h , as C_t/t when t approaches 0, can be defined as:

$$h = kC_s^2. \quad (6)$$

Eq. (5) can be rearranged to obtain:

$$C_t = \frac{t}{\frac{1}{h} + \frac{t}{C_s}}. \quad (7)$$

The initial leaching rate, h , the leaching capacity, C_s , and the second-order leaching rate constant, k , can be determined

experimentally from the slope and intercept by plotting t/C_t against t .

3. Results and discussion

The rate of leaching of water-soluble compounds of *Tilia* sapwood was determined as a function of the temperature using a stirring speed of 100 rpm, a ratio of solids/suspension of 0.14 with 700 ml water, and a particle of size 0.286–0.348 mm. The leaching rate was fast in the beginning of the period and very slow towards the end of the leaching for all temperatures studied (Fig. 2). The initial rapid leaching of water-soluble compounds of *Tilia* sapwood can be attributed to the driving force of fresh water. It is also attributed to the surface of the solid following gradual uptake, which may be due to leaching at the inner surface. The results were analyzed using a second-order leaching model, and these are shown in Fig. 3 as a series of plots of t/C_t against time for the leaching. The agreement of the second-order leaching model with the experimental results confirms our assumptions that there are primarily two phenomena during the leaching of the sapwood of lime: initially there are intense dissolution and scrubbing in which maximum leaching takes place. Then a second, much-slower stage occurs which corresponds primarily to external diffusion and which is related to the soluble remainder.

The saturated leaching capacity, C_s , the leaching rate constant, k , the initial leaching rate, h , and the coefficient of determination, r^2 , are given for various temperatures in Table 1. The initial leaching rate, h , increased with an increase in the temperature and varied from 0.0193 to 0.103 $\text{g L}^{-1} \text{min}^{-1}$, the temperatures changed from 313 to 363 K. Values of the

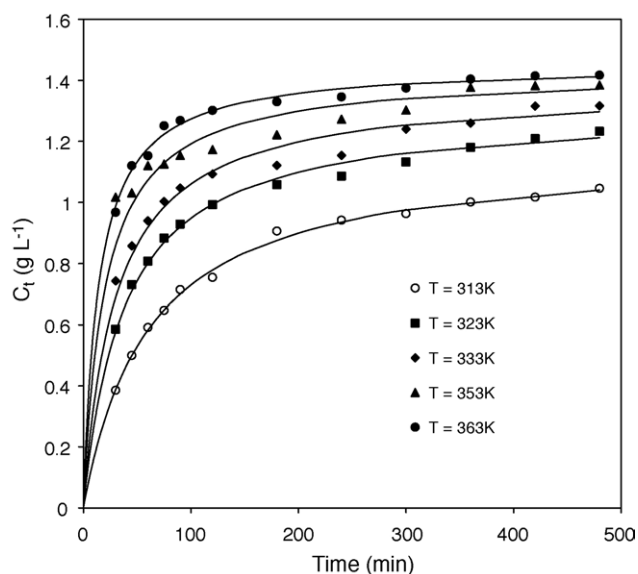


Fig. 2. Plot of water-soluble dry matter of *Tilia* sapwood versus time at various temperatures (ratio of solids/suspension of 0.14, particle size of 0.286–0.348 mm, and stirring speed of 100 rpm).

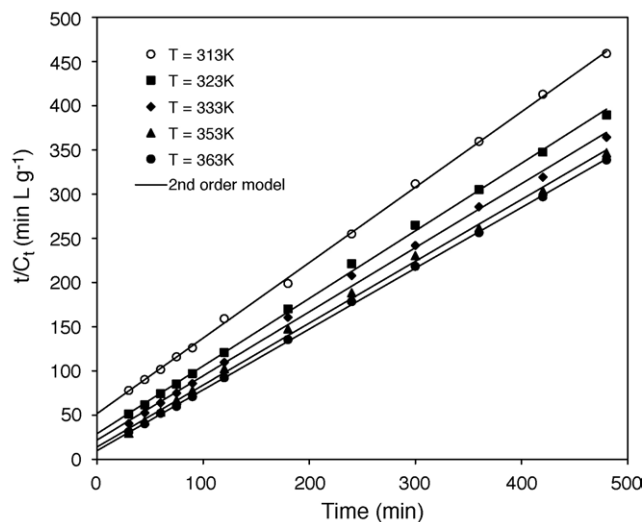


Fig. 3. Second-order leaching kinetics of water-soluble compounds from *Tilia* sapwood at various temperatures (ratio of solids/suspension of 0.14, particle size of 0.286–0.348 mm and stirring speed of 100 rpm).

rate constant, k , were also found to increase from 0.0141 to 0.0486 $\text{L g}^{-1} \text{min}^{-1}$, as well as those of the saturated leaching capacity, which were also found to increase from 1.17 to 1.45 g L^{-1} for an increase in the suspension temperatures of from 313 to 363 K. The increase in the second-order leaching rate constants with increasing temperature may be described by the Arrhenius equation:

$$k = k_0 \exp\left(\frac{-E}{RT}\right); \quad (8)$$

where k is the leaching rate constant ($\text{L g}^{-1} \text{min}^{-1}$), k_0 is a temperature-independent factor ($\text{L g}^{-1} \text{min}^{-1}$), E is the energy of leaching (kJ mol^{-1}), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the suspension absolute temperature (K). The plot of $\ln(k)$ against $1/T$ allows for the calculation of k_0 and E . Values of $\ln(k)$ were plotted as a function of the reciprocal of the absolute temperature, and the linear variation is shown in Fig. 4. There was a linear relationship between the second-order leaching rate constant and the reciprocal absolute temperature with a coefficient of determination of 0.987. Hence, the relationship between k and T can be represented in an Arrhenius form as:

$$\ln(k) = \ln(k_0) + \left(\frac{-E}{R}\right) \frac{1}{T}; \quad (9)$$

Table 1

Linearization of the kinetic model of the second-order leaching at various leaching temperatures of *Tilia* sapwood by water (ratio of solids/suspension of 0.14, particle size of 0.286–0.348 mm, and stirring speed of 100 rpm)

T (K)	C_s (g L^{-1})	k ($\text{L g}^{-1} \text{min}^{-1}$)	h ($\text{g L}^{-1} \text{min}^{-1}$)	r^2
313	1.17	0.0141	0.0193	0.999
323	1.31	0.0202	0.0345	0.999
333	1.38	0.0242	0.0459	0.998
353	1.43	0.0352	0.0719	0.998
363	1.45	0.0486	0.103	1.000

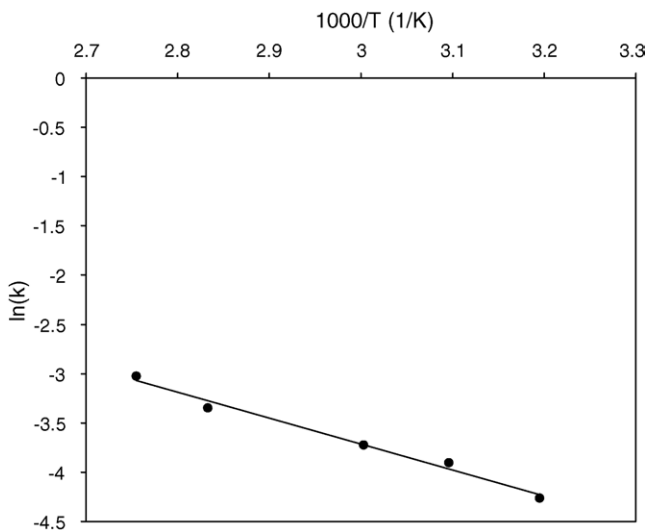


Fig. 4. Relationship between temperature and the second-order leaching rate constant, $\ln(k)$, for leaching of *Tilia* sapwood by water.

where $\ln(k_0)$ is the intercept and $-E/R$ is slope of the plot of $\ln(k)$ versus $1/T$.

$$k = 65.5 \exp\left(\frac{-21.9}{8.314T}\right), \quad (10)$$

From Eq. (10), the constant, k_0 , is $65.5 \text{ L g}^{-1} \text{ min}^{-1}$, and the activation energy for leaching, E , is 21.9 kJ mol^{-1} for water-soluble compounds, showing that the leaching is an endothermic process.

Fig. 5 shows that the trend of the initial leaching rate, h , increased with increasing leaching temperature. A linear relationship between $\ln(h)$ and T with a high coefficient of determination (0.977) was found and is shown in Fig. 6. Values

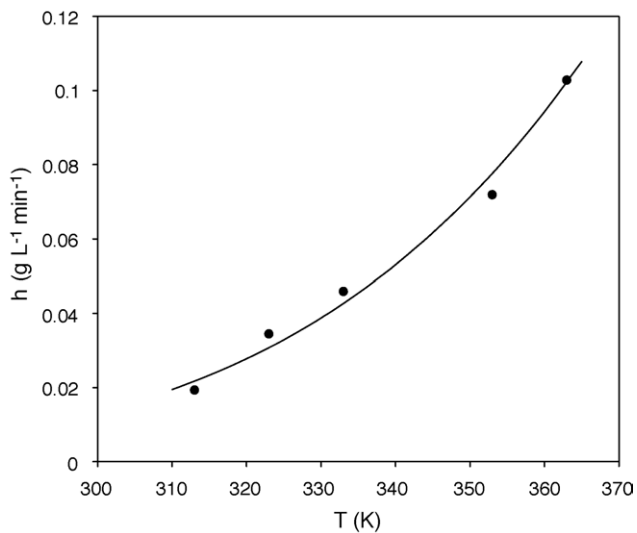


Fig. 5. Relationship between the initial leaching rate, h , and the absolute temperature.

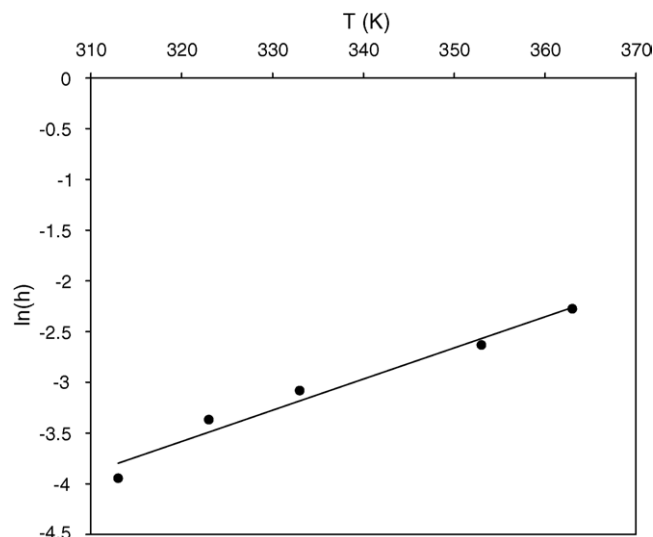


Fig. 6. Linear relationship between the initial leaching rate, $\ln(h)$, and temperature.

of h can be correlated by an empirical equation as follows:

$$h = \exp\left(\frac{-3.52 \times 10^3}{T} + 7.41\right). \quad (11)$$

In addition, C_s values can also be correlated by an empirical equation as follows:

$$C_s = -1.57 \times 10^{-4}T^2 + 1.11 \times 10^{-1}T - 18.2. \quad (12)$$

Fig. 7 shows the relationship between C_s and T with a coefficient of determination of 0.988, and a trend of the saturated leaching capacity, C_s , to increase with increasing leaching temperatures according to the relation of the curve of Eq.

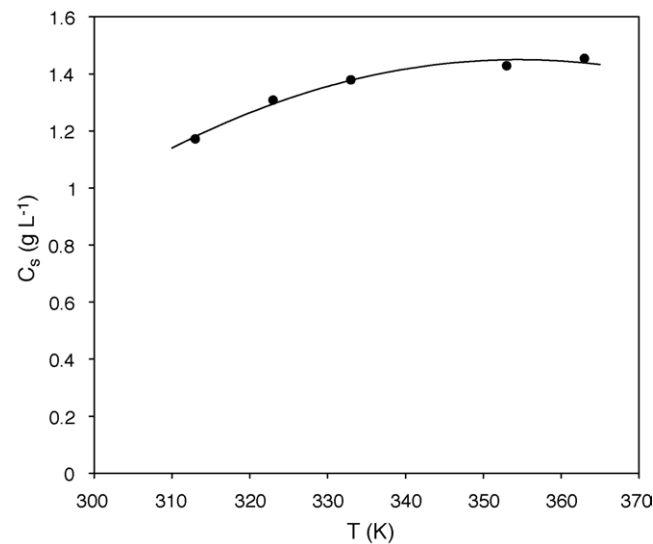


Fig. 7. Relationship between the saturated leaching capacity, C_s , and the leaching temperature.

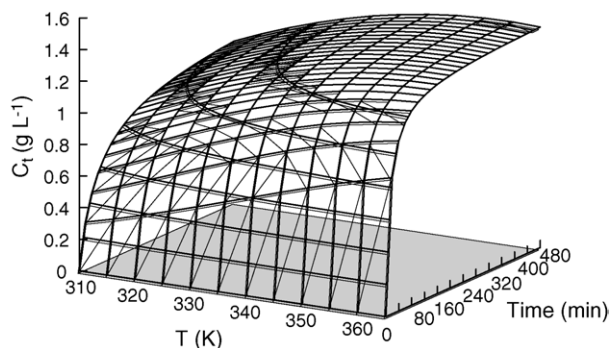


Fig. 8. Predictive model for water-soluble compounds of *Tilia* leached at any leaching time and temperature.

(12) using the experimental data. C_s and h can further be expressed as a function of T . Substituting the values of h and C_s from Eqs. (11) and (12) into Eq. (7), the rate law for a second-order leaching and the relationship of C_t , T , and t can be represented as:

$$C_t = \frac{t}{\exp\left(\frac{3.52 \times 10^3}{T} - 7.41\right) + \left(\frac{t}{-1.57 \times 10^{-4} T^2 + 1.11 \times 10^{-1} T - 18.2}\right)} \quad (13)$$

Empirical Eq. (13) represents the generalized predictive model for the water-soluble compounds of *Tilia* sapwood leached for any leaching time and temperature. It indicates that more water-soluble compounds of *Tilia* sapwood will be leached for any leaching time with a higher leaching temperature. It is obvious that a higher temperature will produce a more efficient leaching process. This equation can then be used to derive the amount of water-soluble compounds of *Tilia* sapwood which can potentially be leached at any given leaching temperature and leaching time. The three-dimensional plot of Eq. (13) is shown in Fig. 8.

4. Conclusion

The kinetics of leaching of water-soluble compounds of the sapwood of *Tilia* were based on the assumption of a mechanism of a second-order leaching that was developed to predict the rate constant of leaching, the saturated capacity of the leaching, and the initial leaching rate. The leaching rate increases with temperature. An activation energy of leaching was evaluated to be 21.9 kJ mol^{-1} water-soluble compounds with the second-order leaching rate constants. A saturated leaching capacity was also evaluated with the second-order leaching rate equation. A three-dimensional predictive model was developed to evaluate the capacity of leaching at all times and temperatures of leaching.

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