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COMPARISON OF KINETIC MODELS FOR THE AQUEOUS SOLID-LIQUID EXTRACTION OF TILIA SAPWOOD IN A CONTINUOUS STIRRED TANK REACTOR

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Comparison of Kinetic Models for the Aqueous Solid-Liquid Extraction of *Tilia* Sapwood in a Continuous Stirred Tank Reactor

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The kinetic study of the aqueous extraction of Tilia sapwood was based on temperature, while all the other factors were kept constant. Several models were used and compared to explain the kinetics of the aqueous solid-liquid extraction of Tilia sapwood. For each model, the rate constant, the equilibrium extraction capacity, and the initial extraction rate were evaluated to analyze the suitability of these kinetic models to describe the leaching process for temperatures ranging from 313 to 363 K. The pseudo first-order model could not be applied during the whole of the process. The Elovich model provided a good degree of correlation (from 0.929 to 0.988) and could be applied all along the extraction process. The pseudo second-order model was satisfactorily applied, with coefficients of correlation over 0.998, showing that it perfectly described the process. A physical explanation of these models was finally proposed.

Keywords Elovich model; First-order model; Kinetics; Leaching; Second-order model; *Tilia* sapwood

Introduction

Different species of *Tilia* can be found depending on of the geographical locations where they grow. *Tilia*, whatever its species or original location, is well known for its therapeutic and cosmetic properties (Viola et al., 1994; Argelas, 1998; Schmidgall et al., 2000; Yildirim et al., 2000; Toker et al., 2001, 2004; Matsuda et al., 2002). The second bark of *Tilia* sapwood contains many molecules of particular interest like sugars, lipids, catechic and gallic tanins, polyphenolic compounds, organic acids, mineral salts, amino acids, vitamins, and essential oils (Baser et al., 1999). These molecules can be separated from their solid vegetable support by leaching. In solid-liquid extraction, a part of the solid is considered as inert and is noticeably insoluble in the solvent. However, the nature of the solid structure can change the

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kinetics of mass transfer. During the extraction and according to Fick's law, the diffusion of the soluble components depends on the gradient of concentration existing between the solid phase (more concentrated) and the liquid phase (less concentrated). This gradient evolves to create an equilibrium between the two phases (Perry et al., 1997), then diffusion becomes negligible even when the contact time is infinitely long under the predetermined conditions. But, when the liquid phase is continuously renewed, the diffusion evolves until the solid phase has been worked out by the solvent.

Matter transfer kinetics is studied in three theoretical stages: (i) putting the solid in contact with the solvent of extraction, which induces a distension of the particles and a solubilization of the compounds, (ii) solid scrubbing with transfer of solute by molecular diffusion from the inside of the solid phase, and (iii) diluting the solute diffused in the solvent to give the extract (Schwartzberg and Chao, 1982). Furthermore, hydrolysis of some water-insoluble compounds is often observed, which leads to additional molecules in the extract. Solid-liquid extraction kinetics has already been studied (Simeonov et al., 1999; Adhikari et al., 2002; Seikova et al., 2004; Wongkittipong et al., 2004), and it has been generally observed that the extraction rate is rapid at the beginning of the process and slows down as equilibrium is approached.

Solid-liquid extraction can be considered as the opposite operation of adsorption (mass transfer of solute between a solid phase and a solvent). The kinetics of extraction seems to be similar to that of adsorption, as shown in a previous paper (Ho et al., 2005a). Thus, the equation used for adsorption can be applied to extraction and such kinetics are often described by a first-order kinetic reaction (Periasamy and Namasivayam, 1996; Kadirvelu et al., 2001; Ho, 2004) and are sometimes interpreted as a combination of two or three different mechanisms (Amacher et al., 1986; Varshney et al., 1996; Comber et al., 1996; Ho and McKay, 1999a; Ho et al., 2005b).

Concerning *Tilia* sapwood, preliminary studies based on the influence of three parameters (temperature, solid-liquid ratio, particle size) were carried out (Adamou et al., 2003, 2005). The kinetic curves, plotted versus these principal parameters, enabled us to conclude that the extraction capacity and the initial extraction rate of extraction increases with the temperature and solid-liquid ratio and decreases with an increase in the particle size, while the stirring speed has little influence on the yield of this extraction. These preliminary studies were carried on by comparing the suitability of three models in order first to describe the kinetics of the solid-liquid extraction of the *Tilia* sapwood in a continuous stirred tank reactor (CTSR) and then explain the mechanism of the process. Thus the efficiency of each model was checked by comparing experimental and calculated parameters like the rate constant, the equilibrium extraction capacity, and the initial extraction rate.

Materials and Methods

Vegetable Material

Tilia sapwood was purchased from Herbo-Chartreuse Company (Saint-Lattier-Grenoble, France). It comes in the form of fibrous rods several centimeters in length. To improve the operation yield, the *Tilia* sapwood was ground before extraction and only particles of 0.348–0.286 mm were used. The complete specifications of the material are shown in Table I. The specific surface was determined by the method

Table I. Physical properties of the *Tilia* sapwood grinding (0.348–0.286 mm) used for the kinetic study

Property	Value
A (Langmuir surface) ($\text{m}^2 \cdot \text{kg}^{-1}$)	1019
Water content (%)	5.46
Ash content (%)	13.76
ρ_a (bulk density) ($\text{kg} \cdot \text{m}^{-3}$)	480
ρ_r (particle density) ($\text{kg} \cdot \text{m}^{-3}$)	818
ε_t (total porosity)	0.412

of adsorption isotherms (Langmuir surface). It was measured by a porosimeter (DEMO 2010 of Micromeritics® type). The water content was determined after drying a precise quantity of *Tilia* sapwood at 80°C until a constant weight was obtained (about 24 hours). The ash content was determined by burning *Tilia* sapwood in an electric furnace of CARBOLITE® type, at 350°C for 24 hours. The ash content is the weight ratio of residue obtained after combustion of the *Tilia* sapwood. The bulk density was obtained by dividing the mass of sapwood grinding by the apparent volume of the bed (volume of the flask). The bulk density (mass grinding/apparent volume, ρ_a) is given by the relation $\rho_a = (m/V_a)$. It was obtained by introducing a precise quantity of *Tilia* sapwood grinding into a graduated flask. The apparent volume was then determined after vibrating the flask for 10 min. The bed porosity (ε_t) was determined by covering the sapwood grinding with hexane in order to fill up the interstitial volume with the solvent. Bed porosity is the ratio of the volume of hexane absorbed on the total volume of hexane plus the grinding volume. Particle density (ρ_r) was obtained according to the relation $\rho_a = \rho_r(1 - \varepsilon_t)$.

Methods

The solid-liquid extraction was carried out in a batch double-jacketed reactor 2 L in volume, equipped with a variable-speed mechanical stirrer (S) and a thermal probe (T). The blade-shaped working part of the stirrer was 7 cm in length and 6 cm in height and was located 6 cm up from the bottom of the vessel. The temperature of the medium was maintained at a constant level by circulating a thermal fluid (glycoled water) within the double jacket of the reactor. A precise amount of deionized water (700 mL) was initially introduced into the reactor and then heated to the temperature studied. A precise amount (98 g) of *Tilia* sapwood grinding (0.286–0.348 mm) was then introduced into the medium, and the mixture was stirred at that temperature for eight hours. The experimental setup of the process, geometric parameters, characteristics of the reactor and impeller are shown in Figure 1.

The influence of the temperature on the extraction kinetics was studied while keeping all the other factors constant. Therefore, these experiments were carried out with a weight ratio of solid to water of 0.14 (other ratios were checked and gave the same trends; this is the best ratio), a particle size of 0.286–0.348 mm (the most important fraction size obtained after sieving the ground sapwood according to the Afnor scale), and a stirring speed of 100 rpm (convenient speed to obtain a good dispersion of the suspension) at 313, 323, 333, 353, and 363 K.

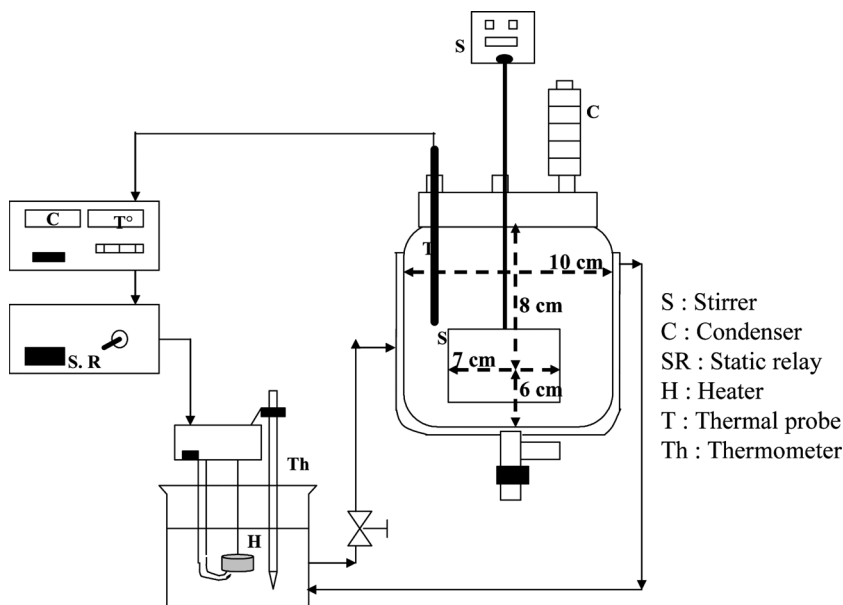


Figure 1. Schematic representation of the continuous stirred tank reactor.

The goal of this operation was to evaluate the dry matter enrichment of the extract, as it was shown in a previous work (Adamou et al., 2003) that the concentration of target molecules was a linear function of the concentration of water-soluble matter. The kinetics of the extraction was monitored by withdrawing 50 mL samples 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 was then calculated. The results were obtained with a standard deviation means (σ) of 0.011, indicating that the method is overall repeatable and precise.

Kinetic Models of Solid-Liquid Extraction

The rate of leaching should be proportional to a driving force, which is assumed to be $(C_s - C_t)$, where C_s (gL^{-1}) and C_t (gL^{-1}) are the concentrations of water-soluble compounds of *Tilia* sapwood at saturation and at any time t respectively. The extraction order and rate constant must be experimentally determined. Several models describing the rate of extraction were studied and compared.

Extraction First-Order Model

The pseudo first-order equation of Lagergren (Lagergren, 1898; Reddad et al., 2002; Ho, 2004) can be rewritten in its differential form as follows:

$$\frac{dC_t}{dt} = k_1(C_s - C_t) \quad (1)$$

where k_1 (min^{-1}) is the first-order extraction rate constant, and t (min) the time.

Equation (1) was integrated with application of the boundary conditions $C_t = 0$ at $t = 0$ and $C_t = C_t$ at $t = t$:

$$\ln\left(\frac{C_s}{C_s - C_t}\right) = k_1 t \quad (2)$$

Equation (2) may be rearranged to obtain the linear form:

$$\log(C_s - C_t) = \log(C_s) - \frac{k_1}{2.303} t \quad (3)$$

The plots of $\log(C_s - C_t)$ against t for different experimental conditions were analyzed to allow a calculation of the constant k_1 from the slope and the equilibrium extraction capacity C_s (concentration obtained at saturation) from the intercept.

Extraction Second-Order Model (Ho et al., 2005a)

The second-order kinetic equation for the extraction rate can be written as follows:

$$\frac{dC_t}{dt} = k_2(C_s - C_t)^2 \quad (4)$$

where k_2 ($\text{Lg}^{-1}\text{min}^{-1}$) is the second-order extraction rate constant.

Separating the variables in Equation (4) gives:

$$\frac{dC_t}{(C_s - C_t)^2} = k_2 dt \quad (5)$$

Subsequently, Equation (8) is obtained by integrating with application of the boundary conditions $C_t = 0$ at $t = 0$ and $C_t = C_t$ at $t = t$ and rearranging the following relations:

$$\frac{1}{(C_s - C_t)} - \frac{1}{C_s} = k_2 t \quad (6)$$

$$C_t = C_s - \frac{C_s}{1 + C_s k_2 t} \quad (7)$$

$$C_t = \frac{C_s^2 k_2 t}{1 + C_s k_2 t} \quad (8)$$

Equation (8) is the integrated rate law for an second-order extraction reaction and can be rearranged again to obtain a linear form:

$$\frac{t}{C_t} = \frac{1}{k_2 C_s^2} + \frac{t}{C_s} \quad (9)$$

The extraction rate (C_t/t) can be obtained from Equation (10) as:

$$\frac{C_t}{t} = \frac{1}{(1/k_2 C_s^2) + (t/C_s)} \quad (10)$$

and the initial extraction rate h , as C_t/t when t approaches 0, can be defined as:

$$h = k_2 C_s^2 \quad (11)$$

Equation (8) can be rearranged to finally obtain:

$$\frac{t}{C_t} = \frac{t}{C_s} + \frac{1}{h} \quad (12)$$

The initial extraction rate h , the extraction capacity C_s , and the second-order extraction rate constant k_2 can be determined experimentally from the slope and the intercept by plotting t/C_t against t .

Elovich Model

The Elovich or Roginsky-Zeldovich equation is generally expressed as follows (Low, 1960; Sparks, 1986):

$$\frac{dC_t}{dt} = \alpha e^{(-\beta C_t)} \quad (13)$$

where α ($\text{g L}^{-1} \text{min}^{-1}$) and β (L g^{-1}) are respectively the initial extraction rate and the extraction rate constant. The integration of $(dC_t/\alpha)e^{(\beta C_t)} = dt$, with application of the boundary conditions $C_t = 0$ at $t = 0$ and $C_t = C_t$ at $t = t$, leads to

$$\frac{e^{(\beta C_t)}}{\alpha\beta} = t + \frac{1}{\alpha\beta} \quad \text{or} \quad e^{(\beta C_t)} = \alpha\beta t + 1 \quad (14)$$

Equation (14) becomes $\beta C_t = \ln(\alpha\beta t + 1)$. To simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha\beta t \gg 1$ and relation 15 is finally obtained:

$$C_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (15)$$

Thus the constants can be obtained from the slope and intercept of the linear plot of C_t versus $\ln(t)$. Equation (15) will be used to test the suitability of the Elovich equation to describe the *Tilia* sapwood aqueous extraction kinetics.

Results and Discussion

When the *Tilia* sapwood grinding was extracted with water as a solvent, the increase in concentration of the extract was rapid at the beginning of the process, then slowed down with time for all the temperatures studied (Figure 2). The evolution of the quantity of water-soluble compounds extracted from *Tilia* sapwood is displayed in the plots of concentration versus time. These results were used to check three kinetic models.

Extraction First-Order Model

The influence of temperature on solid-liquid extraction was studied with five temperatures ranging from 313 to 363 K. The plot of $\log(C_s - C_t)$ versus t (Figure 3) shows that the extraction of water-soluble compounds of *Tilia* sapwood can be represented in a linear form according to the first-order model. From the slope and the intercept of the plot, k_1 , C_s , and the coefficient of determination, r^2 , were calculated (Table II). These results presented generally low coefficients of determination. Furthermore, as shown in Figure 3, the linearization is better at the beginning of the process than at a later stage. Thus, the process does not globally

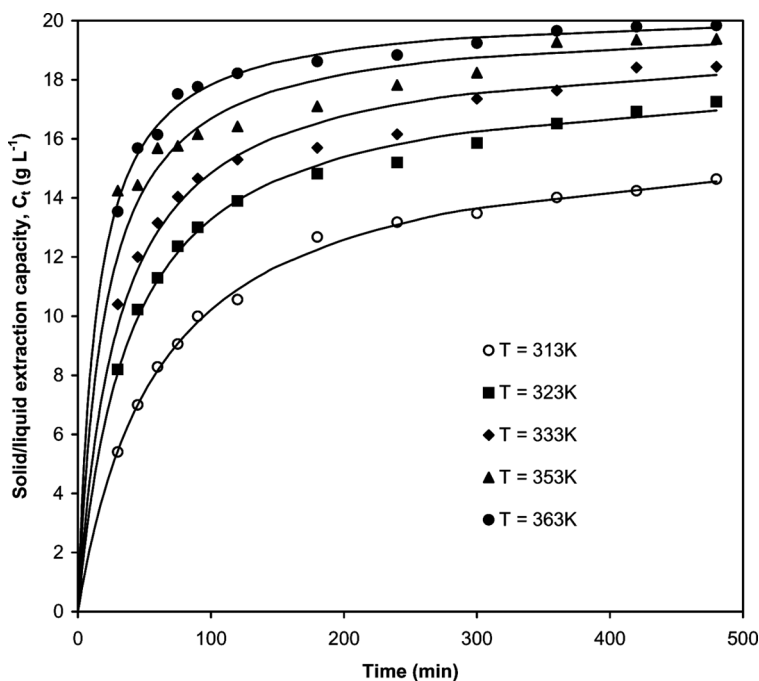


Figure 2. Influence of temperature on the kinetics of the aqueous extraction of *Tilia* sapwood (ratio of solid/solvent 0.14, particle size 0.286–0.348 mm, stirring speed 100 rpm).

follow the evolution of a first-order kinetic model of extraction, although the beginning of the extraction agrees with this order. Indeed, according to Ho and McKay (1999b), few processes give satisfactory results in kinetic studies of pseudo first-order, and this model is applicable only during the first 20 or 30 minutes. Indeed,

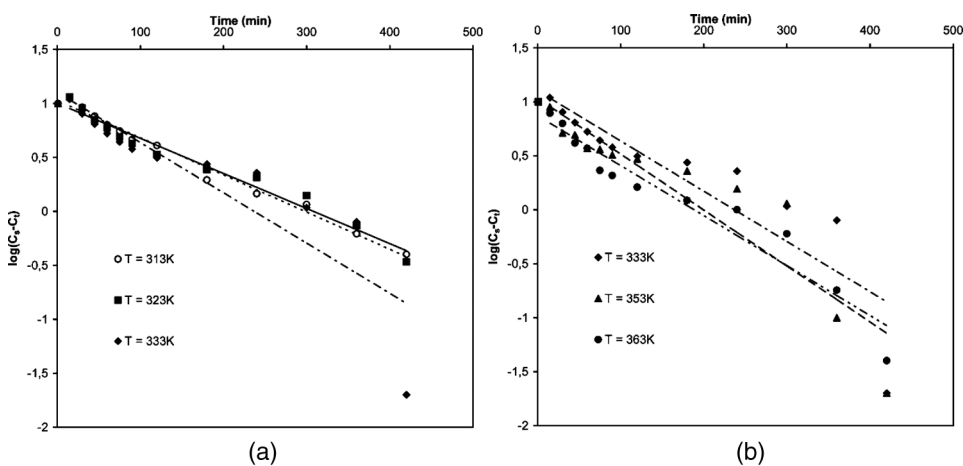


Figure 3. Influence of temperature on the kinetics of the aqueous extraction of *Tilia* sapwood first-order model (ratio of solid/solvent 0.14, particle size 0.286–0.348 mm, stirring speed 100 rpm).

Table II. Linearization of the first-order kinetic model of aqueous extraction of *Tilia* sapwood at various temperatures (ratio of solid/solvent 0.14, particle size 0.286–0.348 mm, stirring speed 100 rpm)

T (K)	Slope* ($\times 10^3$)	k_1 ($\text{min}^{-1} \times 10^3$)	Intercept*	C_s (g L^{-1})	r^{2*}
313	−3.45	7.94	1.027	10.6	0.987
323	−3.25	7.48	1.001	10.0	0.969
333	−4.66	10.7	1.103	12.7	0.782
353	−5.18	11.9	1.033	10.8	0.852
363	−4.63	10.6	0.870	7.41	0.932

*These values were obtained from Microsoft Excel[®].

the process of extraction seems to take place in two stages of pseudo first-order, as shown in Figure 4 for 313 K. In the present study, it was observed that for all the temperatures studied, the first order gave a good correlation up to 90 minutes. Thus, a maximum of matter was dissolved and extracted during the first 90 minutes. After 90 minutes, only the remaining soluble matter was scrubbed from the solid phase. The new values of k_1 and C_s were calculated again from the respective slopes and intercepts before 90 minutes leaching elapsed and are reported in Table III. This table shows that the new first-order rate constants are generally some 50% higher

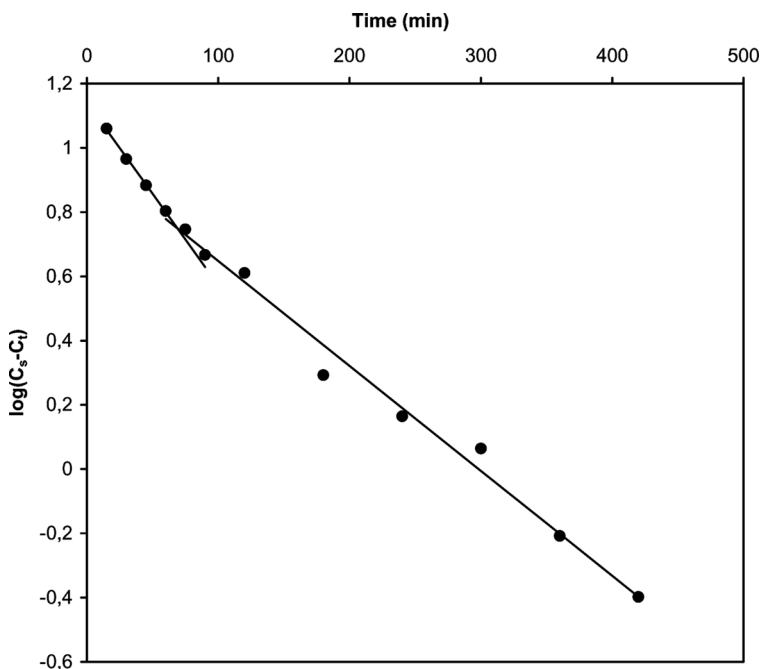


Figure 4. First-order kinetic model for the extraction of water-soluble compounds from *Tilia* sapwood at 313 K (ratio of solid/solvent 0.14, particle size 0.286–0.348 mm, stirring speed 100 rpm).

Table III. Linearization of the first-order kinetic model for a 90-minute aqueous extraction of *Tilia* sapwood at various temperatures (ratio of solid/solvent 0.14, particle size 0.286–0.348 mm, stirring speed 100 rpm)

T (K)	Slope* ($\times 10^3$)	k_1 ($\text{min}^{-1}(\times 10^3)$)	Intercept*	C_s (g L^{-1})	r^{2*}
313	-5.16	11.8	1.125	13.3	0.995
323	-5.77	13.2	1.130	13.5	0.990
333	-6.06	13.9	1.101	12.6	0.986
353	-5.33	12.2	0.945	8.8	0.860
363	-8.05	18.5	1.017	10.4	0.977

*These values were obtained from Microsoft Excel[®].

than those calculated from Table II. In the same way, the extraction capacity is also generally better.

Extraction Second-Order Model

The same data were analyzed by using a second-order kinetic model of extraction. The results are shown as a series of plots of t/C_t against t in Figure 5. The saturated

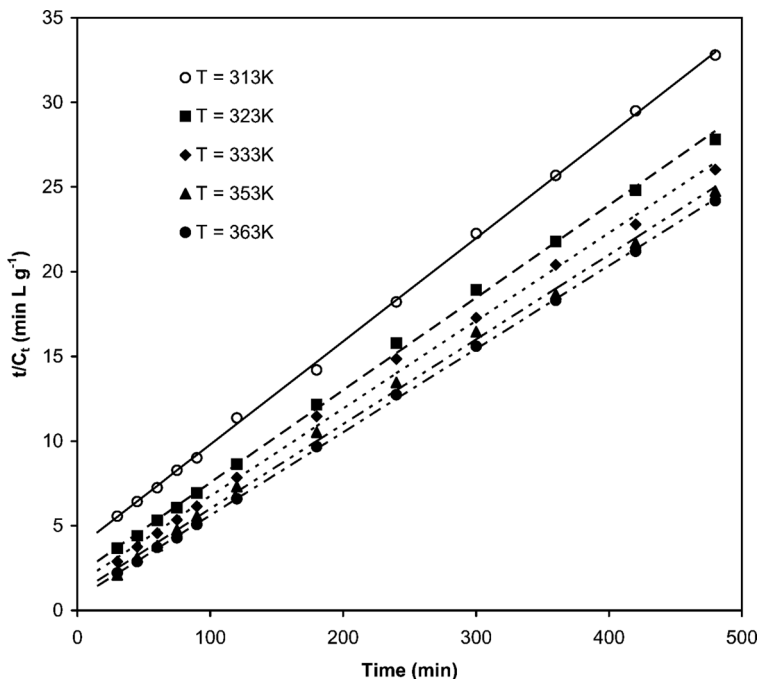


Figure 5. Second-order kinetic model for the extraction of water-soluble compounds from *Tilia* sapwood at various temperatures (ratio of solid/solvent 0.14, particle size 0.286–0.348 mm, stirring speed 100 rpm).

Table IV. Linearization of the second-order kinetic model of the aqueous extraction of *Tilia* sapwood at various temperatures (ratio of solid/solvent 0.14, particle size 0.286–0.348 mm, stirring speed 100 rpm)

T (K)	Slope* ($\times 10^2$)	C_s g L^{-1}	Intercept*	h $\text{g L}^{-1} \text{min}^{-1}$	k_2 $\text{L g}^{-1} \text{min}^{-1} (\times 10^3)$	r^{2*}
313	6.10	16.4	3.69	0.270	1.01	0.999
323	5.46	18.3	2.07	0.483	1.44	0.999
333	5.18	19.3	1.56	0.642	1.73	0.998
353	5.00	20.0	0.99	1.006	2.52	0.998
363	4.91	20.4	0.69	1.439	3.50	1.000

*These values were obtained from Microsoft Excel[®].

extraction capacity, C_s , the initial extraction rate, h , the extraction rate constant, k_2 , and the coefficient of determination, r^2 , given for various temperatures in Table IV, are in accordance with the graphs in Figure 5. The initial extraction rate, h , is multiplied by 5 when the temperature is increased by 50 K, according to the kinetic law. The values of the rate constant, k_2 , were also found to increase from 0.0010 to 0.0035 $\text{L g}^{-1} \text{min}^{-1}$; in the same ways, the values of the extraction capacity were found to increase from 16.4 to 20.4 g L^{-1} as the solution temperature was increased from 313 to 363 K. Compared with the first-order extraction model, the second-order model presents very high coefficients of determination (always above 0.998) and may be used to explain the physicochemical process.

The Elovich Model

With the aim of finding a correlation between experimental data and theoretical data predicted by the model of Elovich, a relationship was established between the concentration of water-soluble dry matter of *Tilia* sapwood, C_t , and $\ln(t)$, for every temperature of Figure 6. Table V presents the kinetic constants obtained from Figure 6. It is possible to observe that the values of the initial extraction rate α and those of the extraction rate constant β increase with temperature and the coefficient of determination remains reasonably good, although it decreases when the temperature increases. In addition, by increasing the temperature from 313 to 363 K, the value of the initial extraction rate, α , increased from 0.624 to 53.8 $\text{g L}^{-1} \text{min}^{-1}$ and the extraction rate constant β increased from 0.295 to 0.457 L g^{-1} . When compared with those of the second-order model, these results are less satisfactory, especially if the temperature exceeds 323 K. Furthermore, like the first-order model, the Elovich model can be divided into two stages, one from 0 to 90 min where the extraction rate constant is higher than in the second stage, starting at 90 min. Table VI presents the new computed values until the 90th minute of extraction. The coefficients of determination are generally good, but the extraction rate constants are about 25% inferior to those in Table V. The initial extraction rate is also inferior, although it is less influenced by the temperature in the linearization than those of Table V. However, the Elovich equation provides a description of solid/liquid extraction of *Tilia* sapwood that is better than that offered by the first-order model but not as good as that given by the second-order model.

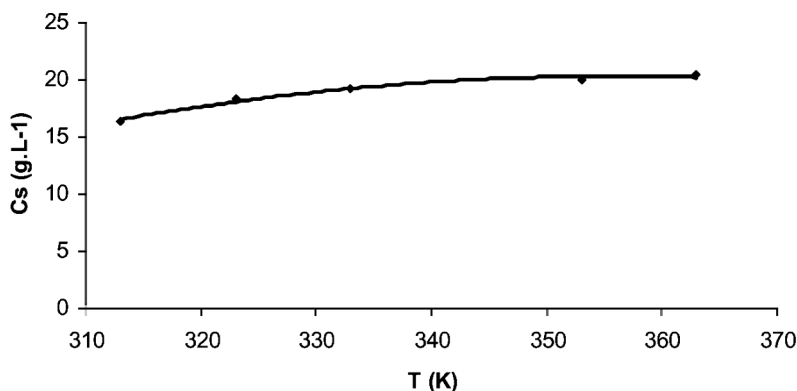


Figure 6. Elovich kinetic model for the extraction of water-soluble compounds from *Tilia* sapwood at various temperatures (ratio of solid/solvent 0.14, particle size 0.286–0.348 mm, stirring speed 100 rpm).

Discussion

The pseudo first-order model did not give satisfactory results, and the plot of $\log(C_s - C_T)$ versus time could be divided into two or more sections. According to Covelo et al. (2004), the model of pseudo first order is appropriate only for a process (adsorption or desadsorption) that has only one mechanism and that is quick and short. Therefore, the experimental results could be represented by two first-order kinetic models of extraction when equilibrium was approached. In a multiple first-order kinetics, the first stage corresponds to the initial removal of the most soluble molecules that are desorbed on the surface with a reorganization of the solid surface. In this stage the interactions between molecules are negligible and lead to the formation of a monolayer as in the adsorption process. The second stage is slower because it is controlled by a diffusion film and an intraparticle diffusion mechanism. The second stage could also correspond to the removal of less soluble molecules and/or a partial hydrolysis of the organic matter (especially polyholosides).

The application of the Elovich model is better, especially for lower temperatures, but the same trends are found as in the first-order model. Generally, this model is

Table V. Linearization for the Elovich equation of the kinetic model of the aqueous extraction of *Tilia* sapwood at various temperatures (ratio of solid/solvent 0.14, particle size 0.286–0.348 mm, stirring speed 100 rpm)

T (K)	Slope*	β $L g^{-1}$	Intercept*	α $g L^{-1} min^{-1}$	r^{2*}
313	3.38	0.295	−5.71	0.624	0.988
323	3.21	0.311	−2.16	1.64	0.980
333	2.96	0.338	0.556	3.57	0.972
353	2.27	0.440	5.65	27.4	0.950
363	2.19	0.457	7.01	53.8	0.929

*These values were obtained from Microsoft Excel[®].

suitable for highly heterogeneous systems and particularly when a physicochemical process occurs.

As compared with the adsorption process, the pseudo second-order model may be satisfactorily applied when the rate-limiting step is a chemisorption involving valency forces between solute and solvent. However, two phenomena occur during the aqueous solid-liquid extraction of *Tilia* sapwood in which maximum extraction takes place: an intense dissolution during the initial first stage and a strong scrubbing of the most soluble molecules (normal extraction) in the second stage. The second stage is much slower because of the problems of transfer of other molecules and of the modification of the solid structure. This stage corresponds essentially to an external diffusion that concerns the soluble matter remainder. According to Covelo et al. (2004), the aptitude of the second degree to describe the kinetics of adsorption or desorption implies the existence of a two-stage process. These authors also mention that the structure of the raw material is able to cause problems of slowness, tortuosity, and mass transfer to explain the suitability of the pseudo second-order model.

When concentration at saturation (C_s) is compared with these models, Tables II and III show that the values of C_s are, on one hand, not clearly influenced by temperature with the first-order model, and these results are inconsistent with an endothermic process. On the other hand, the values of C_s increase with temperature, according to a second-order polynomial function, with the second-order model. These results allow determining the influence of temperature on the external diffusion of solute into the extract by plotting C_s versus time (Figure 7). The values of C_s can be correlated by an empirical equation, with a coefficient of determination of 0.982, as follows : $C_s = -0.002 T^2 + 1.449 T - 237.6$.

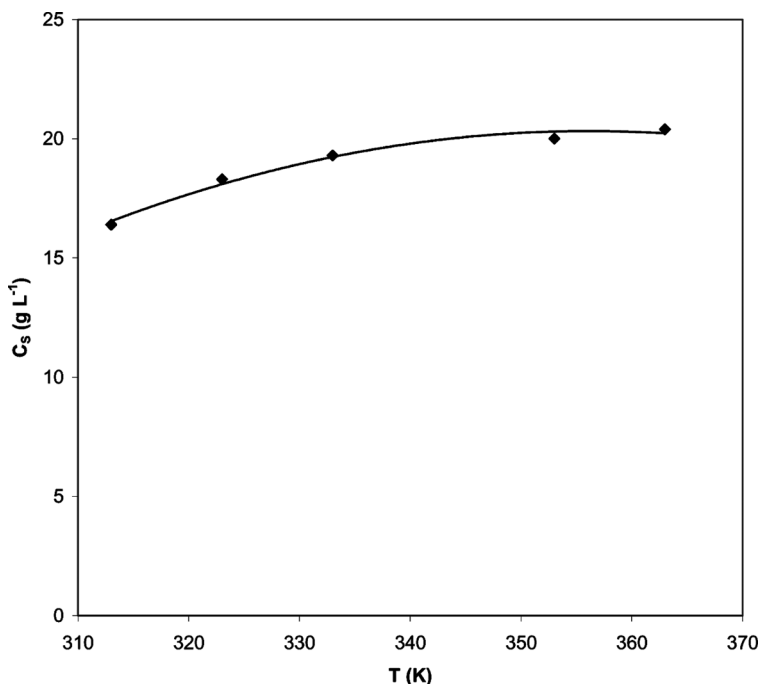


Figure 7. Relationship between the concentration at saturation and the extraction temperature.

Table VI. Linearization of the Elovich kinetic model for a 90-minute aqueous extraction of *Tilia* sapwood at various temperatures (ratio of solid/solvent 0.14, particle size 0.286–0.348 mm, stirring speed 100 rpm)

T (K)	Slope*	β $L g^{-1}$	Intercept*	α $g L^{-1} min^{-1}$	r^{2*}
313	3.82	0.261	-7.39	0.552	0.996
323	4.12	0.242	-5.54	1.07	0.997
333	4.01	0.249	-3.31	1.76	0.999
353	3.05	0.327	2.84	7.75	0.918
363	3.37	0.296	2.62	7.33	0.976

*These values were obtained from Microsoft Excel[®].

Adsorption is a chemical or a physical process that allows binding molecules contained in a liquid or a gas onto the surface of a solid. For a porous solid, the term "surface" also includes the internal area generated by the pores accessible to the solute, which is important as the larger the surface, the better the process. The physical adsorption results from the physical interactions between the atoms constituting the surface of the solid and the molecules of the liquid or gas phase. These interactions are caused by electrostatic forces of Van der Waals type, hydrogen bonds, etc. They have a fast and nonselective action, and they do not cause any modification in the adsorbed molecules. The physisorption is reversible because the equilibrium of the phases varies according to the surface, the porosity of the solid, and the temperature. Chemical interactions between the adsorbed molecules and the adsorbent surface also induce a chemical adsorption. As they are often selective, they can produce irreversible modifications of the adsorbed molecules. Chemisorption is generally promoted by high temperatures because it generates strong energies of adsorption.

The purpose of solid-liquid extraction is to separate one or more molecules contained in a solid phase by dissolution in a solvent. In solid-liquid extraction, a large part of the solid is considered to be inert and is noticeably insoluble in the solvent. This process consists of the mass transfer of a solute between a solid and a liquid phase, which leads to the enrichment of one phase to the detriment of the solid phase according to the three-step mechanism described in the introduction; adsorption acts conversely. As a matter of fact, biosorption processes work through a multistep mechanism, including several processes of mass transfer of solute such as (i) the diffusion of solute in the bulk of the liquid phase, (ii) the diffusion of solute across the liquid film surrounding the solid particles, (iii) the diffusion of solute in the liquid filling the micropores and macropores, and (iv) the binding of solute on the solid surface. However, the physicochemical phenomena may be slightly different in both processes. The main differences affect the surface of the solid and the diffusion of the solute. The surface state of the solid is fundamental with adsorption, because the fixation of solute may be enhanced or reduced according to the physical nature of the surface, and the mechanism may be different according to the chemical structure of the solid. In solid-liquid extraction, the nature of the surface is of less importance since the totality of the solid is concerned by the phenomenon, though, for the same solute, the extraction rate is better with small particles than with the larger one. Nevertheless, the physicochemical properties of the solvent of extraction and

particularly its polarity and viscosity are of prime importance to selectively dissolve the molecules to be extracted and to diffuse them from the solid into the liquid phase. Despite these differences, solid-liquid extraction can be considered as the opposite operation to adsorption, and that is the reason why some authors (Adhikari, 2002) call this operation desadsorption.

Conclusion

In this study, the kinetics of the solid-liquid extraction of *Tilia* sapwood was explored experimentally, and the results were checked by using three models. The established theoretical equations were used to correlate the experimental data for the kinetics of the extraction at various temperatures. The results allow assuming that the leaching of water-soluble compounds of *Tilia* sapwood works out according to a pseudo second-order model, similar to the models obtained in chemisorption processes with valency forces between solvent and solute. Therefore, it may be assumed that the leaching of water-soluble compounds follows the same kinetic model as adsorption, the opposite process. Moreover, partial hydrolysis of organic matter may also have to be considered.

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Nomenclature

A	Langmuir surface, $\text{m}^2 \cdot \text{kg}^{-1}$
C_t	concentration of water-soluble compounds at time t , g L^{-1}
C_s	extraction capacity or concentration of water-soluble compounds at saturation, g L^{-1}
h	initial extraction rate, $\text{g L}^{-1} \text{min}^{-1}$
k_1	extraction first-order rate constant, min^{-1}
k_2	extraction second-order rate constant, $\text{L g}^{-1} \text{min}^{-1}$
t	time, min

Greek Letters

α	initial extraction rate, $\text{g L}^{-1} \text{min}^{-1}$
β	extraction rate constant, L g^{-1}
ε_t	bed porosity, dimensionless
ρ_a	bulk density, $\text{kg} \cdot \text{m}^{-3}$
ρ_r	particle density, $\text{kg} \cdot \text{m}^{-3}$

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