Environmental Engineering and Management Journal April 2018, Vol.17, No. 4, 827-839
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

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MASS TRANSFER IN SOLID-LIQUID EXTRACTION AT HIGH SOLUTE CONCENTRATIONS

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Abstract

The solid-liquid extraction process and some of its influencing factors such as solid-liquid ratio, temperature and salt initial amount have been investigated. Also, mathematical modeling for mass transfer coefficients calculation was applied.

An inert porous solid material (coal), impregnated with 10% and 20% mass NaCl or 15% and 30% mass $CaCl_2$, was used. The leaching was conducted in a fixed bed column, in laminar flow. The $CaCl_2$ impregnated samples were investigated in a column with a height/diameter ratio of 2.5, at 20ºC, 30ºC, and 40ºC and the NaCl samples, in a 4.16 height/diameter ratio column, at 30ºC, 40ºC, 50ºC, 60ºC. In both cases, liquid flow rates of 3.8 L/h, 7 L/h, 10.6 L/h, 13.3 L/h were used.

An increase of the extraction degree with the washing liquid flow rate (up to 10.6 L/h) indicated that the solid-liquid ratio is a crucial factor. Temperature increase has a positive influence on the extraction degree.

At the beginning of the process, the salt quantity extracted from the high salt amount sample, using the lowest water flow rate has a similar value to the one extracted from the low salt amount sample, using the highest flow rate. At larger time values ($t > 500$ s), the extraction degree dependence on the liquid flow rate is similar for the high and low salt samples.

Based on the proposed mathematical model, mean time mass transfer coefficient values $k \cdot a$ were calculated and compared to the experimental obtained data.

Key words: diffusion, porous materials, kinetics, liquid- solid extraction, mass transfer coefficient

Received: May, 2017; Revised final: February, 2018; Accepted: March, 2018; Published in final edited form: April 2018

1. Introduction

Studies of a primary separation process of some components from a mixture in a solid matrix subjected to contact with a suitable liquid medium, have found applications in various processes such as metallurgical (Cojocaru et al., 2017; Kim et al., 2009; Nagaphani Kumar et al., 2010; Padilla et al., 2008; Predescu et al., 2017; Sokić et al., 2009; Xu et al., 2010), food, pharmaceutical and cosmetics industries (Bucić-Kojić et al., 2007; Chetan and Rastogi, 2013; Evon et al., 2009; Jerman et al., 2010; Librán et al., 2013; Loginova et al., 2011; Radojkovic et al., 2012; Simeonov and Koleva, 2012; Tzima et al., 2014; Vázquez et al., 2012; Vítková et al., 2011; Wu et al., 2011), as well as environmental protection and biotechnology (Bucar et al., 2013; Costa et al., 2015; Galvín et al., 2012; Grathwohl and Susset, 2009; Sun et al., 2008; Wijngaard and Brunton, 2010; Wijngaard et al., 2012) or metal recovery (Kumar, 2014).

As a result of the diversity of the applicability areas, there are numerous studies focused on process kinetics, modeling and optimization, and also, on factors that influence the solid-liquid extraction (Bucić-Kojić et al., 2007; Chetan and Rastogi, 2013; Evon et al., 2009; Jerman et al., 2010; Librán et al., 2013; Loginova et al., 2011; Padilla et al., 2008, Radojkovic et al., 2012; Simeonov and Koleva, 2012;

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Sokić et al., 2009; Wu et al., 2011). The solid-liquid extraction characterization is difficult due to the high number and type of influencing factors: the form of solid particles, the pore structure and size, the amount of substance to be extracted that varies from particle to particle, but also, during the process, the solid / liquid phase ratio, the type of liquid solvent used, the variation of its concentration, the temperature and the extraction method.

There are good extraction methods for the separation of compounds from ores, but not as effective for the extraction of plant or animal constituents.

In practical terms, there is a great interest in the extraction of higher quantities of the desired compound (solute) in the shortest time period and with reduced costs. Extraction speed is one of the criteria considered when an extraction method is applied (Bucić-Kojić et al., 2007; Radojkovic et al., 2012; Senol and Aydin, 2006). Its value is limited by the mass transfer at the small pores level. The intensity of mass transfer is determined on one hand, by the mass transfer coefficient, the mass transfer area which depends on the form of solid particles, the pore geometry and the contact method and, on the other hand, by a number of other operating factors.

Mathematical modeling allows optimization, simulation and evaluation of mass transfer coefficients and effective diffusion coefficients (Espinoza-Perez et al., 2007; Jokić et al., 2010; Larrard et al., 2010; Nayl et al., 2014; Padilla et al., 2008; Reinheimer et al., 2014; Senol and Aydin, 2006; Tiruta-Barna et al., 2006). Most mathematical models take into account the following stages of solid-liquid extraction process:

- Solvent transfer from the liquid bulk to the surface of the solid;
- Solvent penetration into the solid matrix;
- Liquid phase diffusion in the solid matrix over an increasing distance, depending on the particle shape and porous material structure;
- Solubilization of valuable component from the solid matrix;
- Solute diffusion from the solid phase (intraparticle diffusion);
- Migration of the solute from the liquid surface into the liquid bulk.

This work focuses on the experimental results obtained for the $CaCl_2$ and, respectively, NaCl extraction from a porous carbon matrix, using demineralized water as a solvent.

The research aim was to investigate some extraction influencing factors such as the rate and the extent of extraction, the temperature, the solid / liquid ratio and the initial amount of salt in the solid sample. A self designed set-up, with a fixed bed column, was used to obtain experimental data and use them to perform process optimization using mathematical modeling and calculate the mass transfer coefficients.

2. Material and methods

The solid-liquid extraction in a fixed bed was investigated using an experimental set-up, presented in Fig. 1, consisting of a thermoresistant glass column (1) with an inner diameter of 0.036 m and total height of 0.2 m. The column has a thermo-resistant glass mantle (1a) for the heating liquid (20-60°C). The fixed bed (1c), which contains the sample to be extracted, is made from active charcoal particles with d = 3.0 mm and l = 3.5-4 mm. It is supported by a stainless steel sieve (1b), fixed at the bottom of the column.

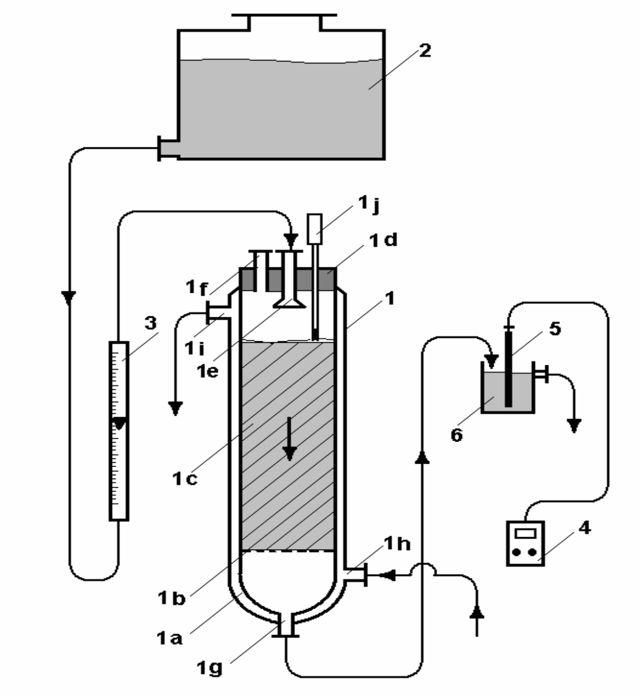

Fig. 1. Experimental set-up

The sample was washed with demineralized fresh water measured using a flowmeter (3). At the column input and output of the liquid phase, the temperatures were measured with digital thermometers with an accuracy of ±0.1 degrees. At the top, the column is covered with a rubber stopper (1d), provided with three inlets for the solvent distribution (1e), a thermometer (1j) and a connection with the outside (1f). The liquid phase resulting from extraction is removed through the connection located at the bottom of the column (1g). Investigations were conducted at atmospheric pressure. Every 30 seconds, the conductivity of the solution obtained after the solvent passed the porous solid bed, was measured.

Extraction of the solid-liquid in a fixed bed was investigated on charcoal samples in the form of cylindrical granules, impregnated with a solution of $CaCl_2$ with two concentrations (15% and 30%) and a NaCl solution of 10% and respectively, 20% concentration, resulting in samples with different concentrations of salt (for NaCl: C_1 = 0.08726 g NaCl/g coal, C_2 = 0.151203 g NaCl/g coal; for $CaCl_2$: C_1 = 0.1334 g $CaCl_2$/g coal, C_2 = 0.2884 g $CaCl_2$/g coal). The height of the active carbon fixed bed was 90 mm for the calcium chloride - impregnated coal and 150 mm for the sodium chloride - impregnated coal. For samples impregnated with $CaCl_2$, three temperature values of 20ºC, 30ºC and respectively, 40ºC were used, the flow of demineralized water was 3.8 L/h, 7 L/h, 10.6 L/h, 13.3 L/h, and the layer height/diameter ratio (H/D) was 2.5. For samples impregnated with NaCl, the investigation was done at 30ºC, 40ºC, 50ºC, 60ºC, with flow rates of 3.8 L/h, 7 L/h, 10.6 L/h, 13.3 L/h and the ratio H/D = 4.16.

Mathematical model

The degree of extraction i.e. the leaching degree, defined by the extracted quantity of calcium chloride (which has passed from the solid into the water), related to the calcium chloride mass which was initially in the extracted solid sample, is calculated with the Eq. (1):

$$\eta = \frac{M_v \rho}{m_s^0 x_A} \sum_i \overline{Y}_{A,i} \Delta t_i \qquad (1)$$

where: $\overline{Y}_{A,i} = \frac{c_{A_i}}{\rho_l - c_{A_i}}$

The extraction rate i.e. the leaching rate, defined as the calcium chloride mass extracted from the sampling bed unit per unit of time, is given by the Eq. (2):

$$v_e = \frac{M_v (c_{A_{i-1}} - c_{A_i})}{V_{ST}} \qquad (2)$$

For the mathematical modeling, the following aspects were taken into consideration:

- the extracted salt diffusion takes place according to the second Fick's law (see Eq. 3),

$$N_A = k \cdot A(c_A^* - c_A) = k \cdot a \cdot V_{ST}(c_A^* - c_A) \qquad (3)$$

where:

- mass transfer surface was written as a product between the specific area, *a*, and the solid bed volume, V_{ST};
- particles retain their shape and size;
- all particles have the same specific surface;
- the liquid flow is laminar;
- the transfer surface is perfectly wetted by the liquid;
- the salt concentration is the same at any point in the liquid phase.

The transferred flux can be expressed also as a minute solute concentration time variation over the bed volume, as in the Eq. (4):

$$\frac{V_{ST}\, dc_A}{dt} = N_A = kA(c_A^* - c_A) \qquad (4)$$

Integrating the Eq. (4), between the limits $t = 0$; $c_A = c_{A0}$ and $t = t$; $c_A = c_A$,

$$\int_{c_{A0}}^{c_A} \frac{dc_A}{(c_A^* - c_A)} = k \frac{A}{V_{ST}} \int_0^t dt \qquad (5)$$

The solid-liquid extraction mathematical model is attained (Eq. 6):

$$\ln\left(c^*_A - c_A\right) = -\frac{kA}{V_{ST}} t + \ln\left(c^*_A - c_{A0}\right) = -k \cdot a \cdot t + \ln\left(c^*_A - c_{A0}\right) \qquad (6)$$

According to the Eq. (6), when a representation of $\ln(c_A - c^*_A)$ as a function of *t* was performed, the obtained slope, *tgα*, is given by the Eq. (7),

$$tg\alpha = k \cdot a \qquad (7)$$

and contains the mass transfer coefficient value, *k*, which can be expressed, based on the Eq. (6), using the Eq. (8):

$$k \cdot a = \frac{1}{t} \ln \frac{(c_A^* - c_{A0})}{(c_A^* - c_A)} \qquad (8)$$

All variables are presented below:

η - extraction degree (leaching degree), dimensionless;

M_v - liquid flow rate (demineralized water) at the entrance in the sampling bed, m^3/s;

ρ - demineralized water density, kg/m^3;

m_s^0 - solid mass of the sampling bed at the initial moment, kg;

x_A - salt mass fraction from the sampling bed at baseline;

$\overline{Y}_{A,i}$ - salt concentration in the liquid phase at the exit from the bed (kg salt/kg water);

Δt_i - the period between the two readings, s;

$c_{A_{i-1}}, c_{A_i}$ - salt concentrations at the bed exit, kg/m^3;

V_{ST} - solid bed volume, m^3;

v_e - extraction rate (leaching rate), kg/m^{3}s;

ρ_l - density of the liquid phase out of the sampling bed, kg/m^3;

k - mass transfer coefficient, s^{-1};

A - mass transfer surface (external and internal of the porous solid particle), m^2;

a - specific surface of the porous solid particles, m^2/m^3;

c_A - extracted salt concentration at equilibrium, kg/m^3;

c_{Ai} - extracted salt concentration at the moment i, kg/m^3;

c_{A0} - extracted salt concentration at the initial moment, kg/m^3;

t - extraction time, s.

3. Results and discussion

3.1. Influence of water flow on extraction degree

The degree of extraction was calculated, using the Eq. (1) for concentration values c_i of the salt in the liquid phase, corresponding to the values of conductivity measured in the discharged liquid from the bottom of the column (1) after passing the sampling bed, using calibration graphs obtained at the experimental temperature.

The calculated extraction degree values, using the Eq. (1), were tabulated and graphically represented. From Figs. 2, 3 and 4 one can observe the extraction degree increase at the same time with the washing liquid flow rate increase, but at values greater of 10.6 L/h, the liquid flow rate influence on the extracted salt quantity is decreasing, very small differences being recorded for t > 700 s at the $CaCl_2$ extraction, while for the NaCl extraction, the smallest differences are recorded for the first extraction stage (t < 500 s). The difference between the values obtained for the extraction degree at 30°C from the coal samples impregnated with 30% $CaCl_2$ solution is significantly higher compared to the difference between the values obtained for the extraction at 30°C from the coal samples impregnated with the solution of 15% $CaCl_2$ (Figs. 2 and 3). The extraction degree profile is different, depending on the initial amount of salt from the sample. This could be explained by the way the extraction mechanism is carried out.

In the first stage, at t < 500 s (for large flow rate values, even at small time values), the salt is washed from the particle exterior by molecular diffusion and convection, afterwards the salt diffusion begins from within the porous particles towards the outside, in the liquid mass. At this stage, the extraction process is determined by a number of factors such that: the solid-liquid contact manner, the process temperature (through its influence on the density and viscosity of the liquid phase), the liquid phase flow rate and the solid granules form.

For the samples with large initial salt concentration, in the time range of t = 500 - 1600 s, the extraction of the largest salt amount, mainly from the large pores, is taking place, after which (at a time longer than 1600 s) the salt extraction from medium and small pores takes place. The medium and small pores extraction is slow and is determined by the solid particles size, porosity and pore shape. For samples with low initial salt concentration, the extraction time for the salt from the large pores is longer.

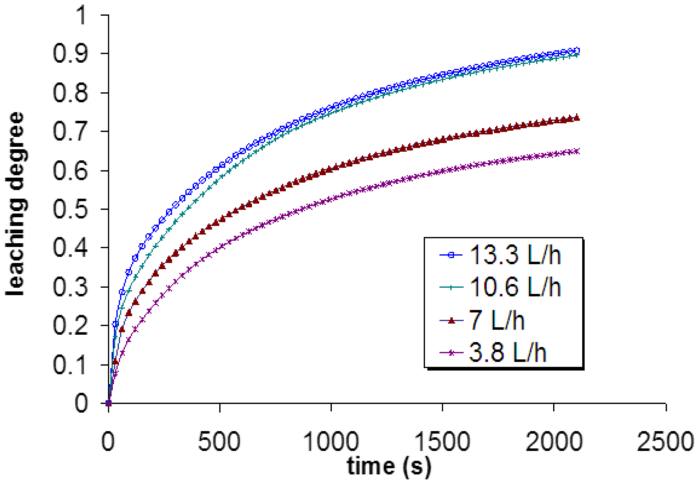

Fig. 2. Extraction degree at 30°C and different liquid flow rates, for the extraction from the samples with $CaCl_2$ C_2 concentration

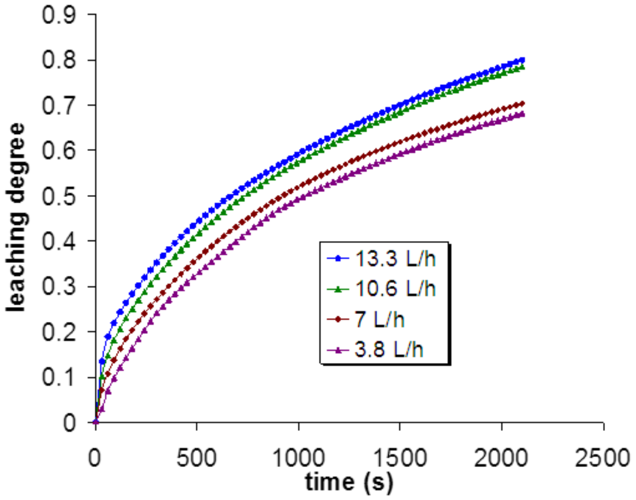

Fig. 3. The extraction degree at a temperature of 30°C and different liquid flow rates, for a C_1 $CaCl_2$ sample concentration

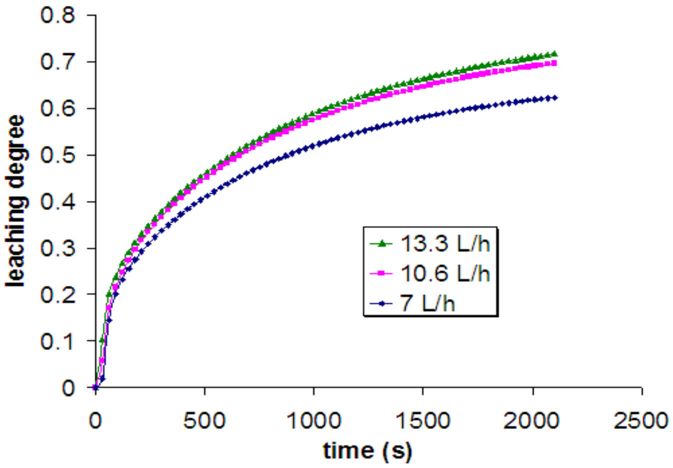

Fig. 4. Extraction degree at a temperature of 40°C and different liquid flow rates for NaCl C_2 sample concentration

The extraction process is completed within a time period slightly larger than 2100 s. The curves profile in Figs. 2, 3 and 4, indicate that the extraction time extent will be much higher for samples with lower initial salt amount. For the NaCl extraction, the extraction curves overlap for the 0-210 s time period which corresponds to the washing stage of porous granules exterior surface. For larger extraction periods, the profiles are similar to the previous ones.

3.2. Influence of temperature on extraction rate

On one hand, temperature increase has a positive influence on the extraction rate due to the washing liquid viscosity decrease, fact that causes an intensification of the particle external diffusion and, on the other hand, due to the increased diffusion coefficient in the solid pores, as one can observe in Fig. 5.

At the largest liquid flow rate (13.3 L/h) one can observe an increase in the extraction degree up to a temperature of 30ºC, afterwards, a temperature increase up to 40ºC determines a decrease of the extraction degree (Figs. 6, 7). This could be due to the decreased solid – liquid contact time. A temperature increase causes a stronger diffusion, and, at the same time, a significant decrease in viscosity, which leads to a reduction of the liquid phase - solid granules contact time.

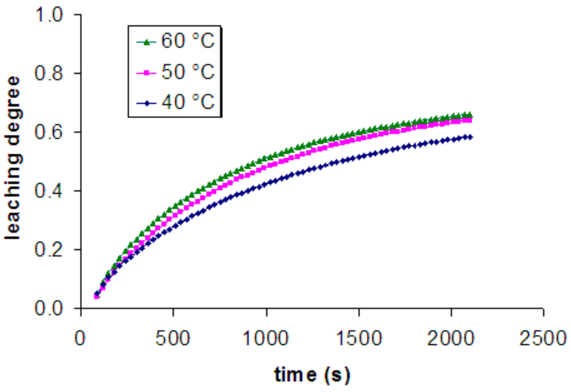

Fig. 5. Extraction degree at a liquid flow rate of 7 L/h and different temperatures for NaCl C_1 sample concentration

As a result of the contact time decrease, the extracted salt amount will be reduced despite the increased diffusion coefficient due to a higher temperature, which suggests that the contact time influence is more important than the one of the diffusion coefficient.

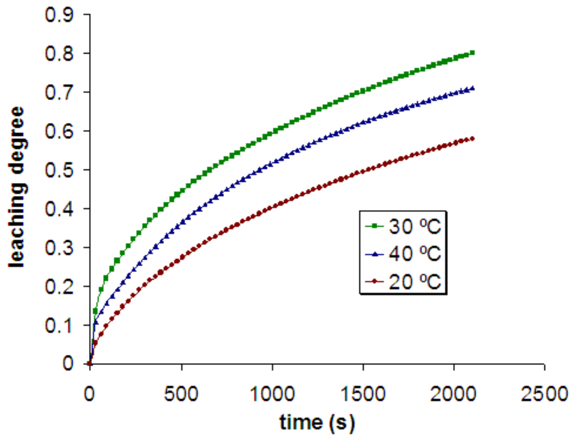

Fig. 6. Extraction degree at 13.3 L/h and three different temperatures, for $CaCl_2$ C_1 sample concentration

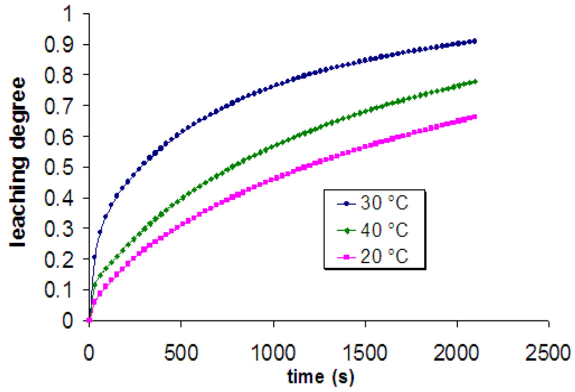

Fig. 7. Extraction degree at different temperatures and 13.3 L/h liquid flowrate, for $CaCl_2$ C_2 sample concentration

3.3. Influence of the salt amount on extraction degree

Fig. 8 summarizes the extraction degree for the minimum (3.8 L/h) and maximum (13.3 L/h) liquid extraction flow rates during the extraction from the samples containing different amounts of the initial salt.

In the first stage (at small time values) the amount of the extracted salt from the sample richer in salt using a water minimum flow rate is close to the one extracted from the sample with a lower salt amount using a maximum water flow rate. In the second stage (time greater than 500 s) the water flow rate influences the values of the extraction degree in a similar manner for the two samples. Also, the slope of the extraction degree variation with time is higher in samples with greater amount of salt (0.2884 g $CaCl_2$/g coal), for the first extraction stage (t < 500 s) and decreases in the second stage when compared to the samples with smaller amount of salt (0.1334 g $CaCl_2$/g carbon).

From Fig. 9, one can observe that an increase of the amount of NaCl by 1.73 times (for samples impregnated with 10% and 20% NaCl solution, respectively, a mass ratio of 0.08726 g NaCl/g coal and 0.151203 g NaCl/g coal, respectively, was determined) leads to an increase of the extracted salt by 1.3 times, under the same conditions of water flow rate, temperature and extraction time (from the maximum value of 0.4782 for the samples with small amount of NaCl to the maximum value of 0.6236 for higher NaCl concentration samples).

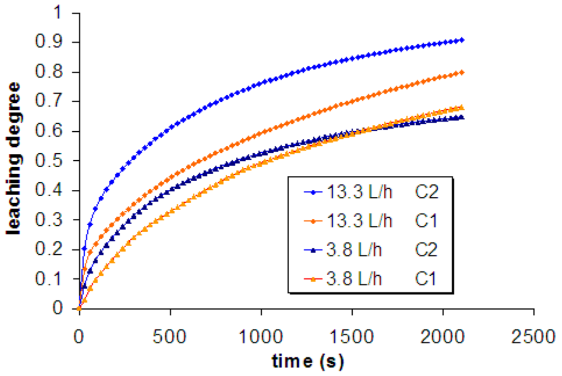

Fig. 8. The extraction degree at 30°C, at 3.8 L/h and 13.3 L/h liquid flow rates, for $CaCl_2$ C_1 and C_2 sample concentrations

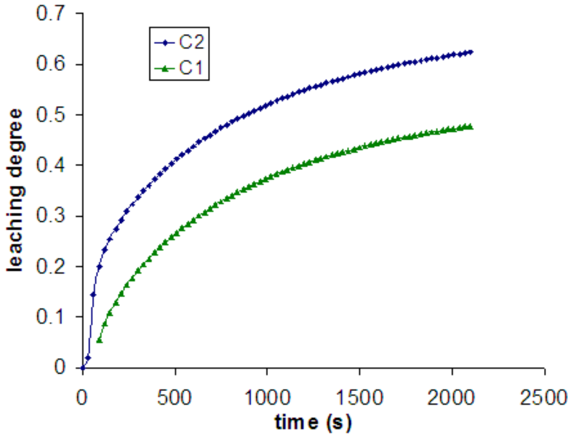

Fig. 9. The extraction degree, for a 7 L/h flow rate and 40°C, for C_1 and C_2 NaCl sample concentrations

3.4. Influence of the fluid flow on extraction rate

Studying the variation of the extraction rate obtained when the equation (2) is applied to the experimentally determined values, one can observe that it reaches a maximum, at small values of the extraction time, typically within the first 250 s, as seen in Figs. 10, 11. The maximum values are influenced by the demineralized water flow rate used to wash the salt. The higher the flow rate, the greater the peak recorded for the extraction rate. The peak obtained at the beginning of the extraction is tall and narrow for large flow rates and decreases in height, becoming wider, as the flow rate decreases. At larger time values, the flow rate does not significantly influence the rate of extraction.

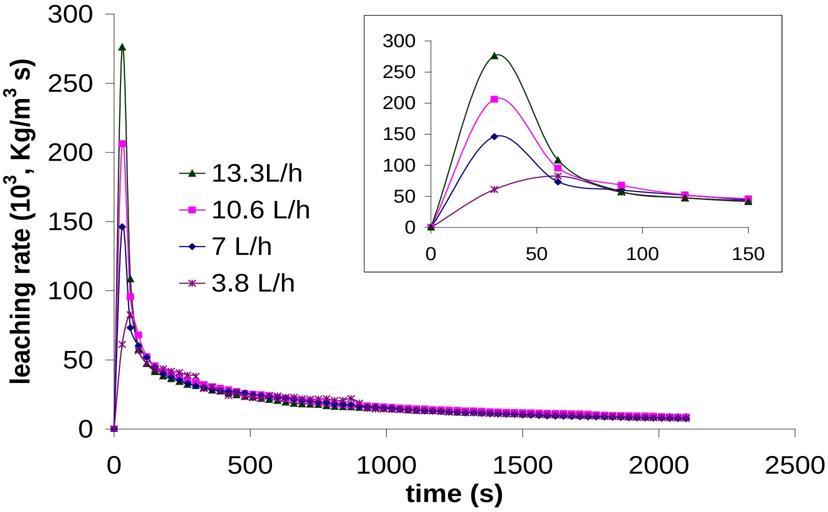

Fig. 10. Extraction rate at 30°C and different liquid flow rates for $CaCl_2$ C_1 sample concentration

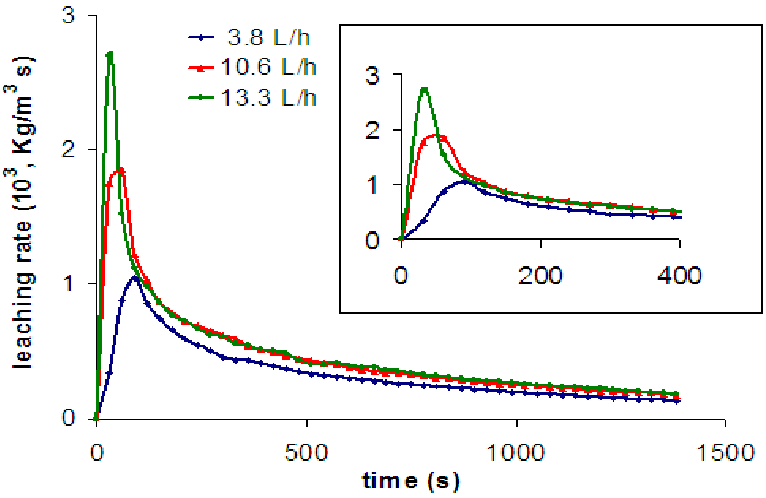

Fig. 11. Extraction rate at 40°C and different flow rates, for the NaCl C_1 sample concentration

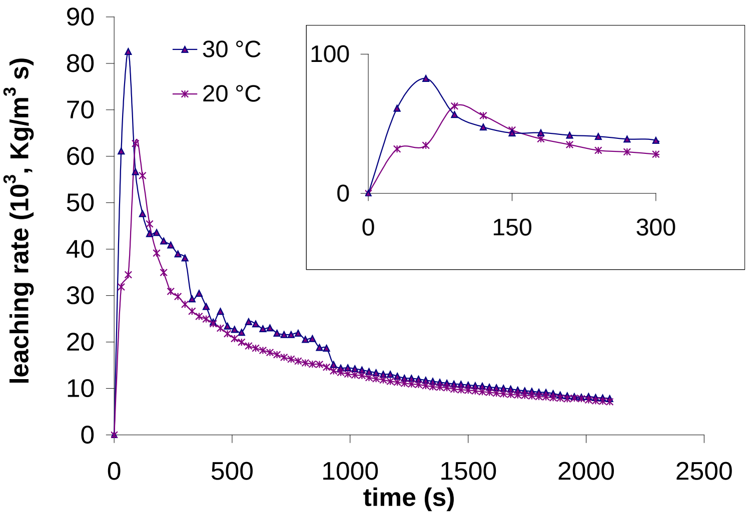

Fig. 12. Extraction rate at small liquid flow rates (3.8 L/h) and different temperatures, for the $CaCl_2$ C_1 concentration samples

Two stages of extraction can be distinguished:

1. In the first stage, corresponding to a range of 0-500s, the particle is washed on the outside and the process rate is determined by the washing demineralized water flow rate.
2. In the second stage, at times greater than 500 s, the diffusion inside the active carbon particle is decisive for the extraction, such that the liquid phase flow rate value influences to a lesser extent the extraction process rate.

3.5. Influence of temperature on extraction rate

The temperature increase has a double positive influence, on one hand on the liquid viscosity and on the other hand on the diffusion coefficient, both causing an intensification of the extraction process. Thus, the process takes place even at low liquid flow rates, as shown in Fig. 12. At a high flow rate, the extraction process rate is determined by the contact time between the solid - liquid phases, the obtained data rendered an optimum extraction temperature of 30^{o}C, as indicated in Fig. 13.

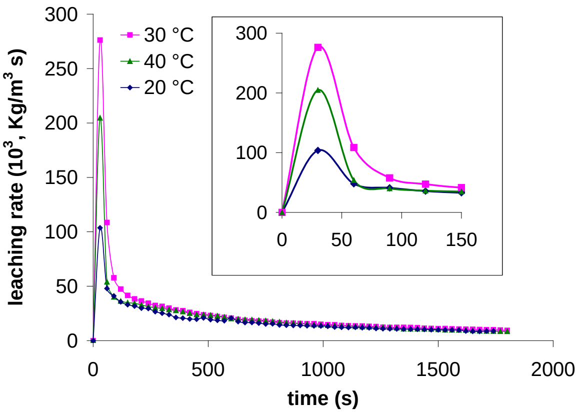

Fig. 13. The extraction rate at 13.3 L/h and different temperatures, for the C_1 $CaCl_2$ concentration samples

3.6. Variation of extraction rate with sample salt amount

Figs. 14 and 15 show the extraction rate variation with respect to the increase in the initial sample salt amount. For a NaCl sample increase by 1.73, the extraction rate at 40°C increases by 5.12 times, at a flow rate of 3.8 L/h and by 3.91 times, at a flow rate of 10.6 L/h, as shown in Fig. 14. A positive influence of the initial salt amount in the sample on the extraction rate is recorded at $CaCl_2$ extraction too. In Fig. 15, the $CaCl_2$ extraction rate, at 30°C, with a flow rate of 13.3 L/h demineralized water, is shown. For a sample salt amount increase by 2.16 times, an increase in the extraction rate by 4.1 times is recorded.

All of the above measurements were performed twice or, for some investigated parameters, even three times, the data reproducibility was very good, with a difference of maximum 1% between two runs of identical parameter values.

To our best knowledge, there is no literature study that investigates the NaCl or $CaCl_2$ leaching from impregnated coal, at large solute concentrations, thus, we could not render any comparison to other experimental data. However, leaching experiments, performed on other systems (Bouffard and Dixon, 2009; Srithammavut et al., 2011), and the obtained leaching degree/rate curves in time indicate similar behaviors to our study.

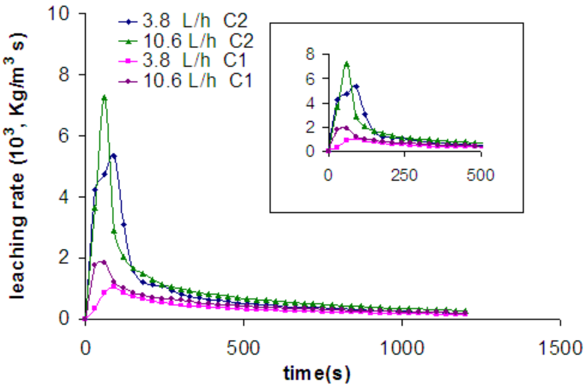

Fig. 14. The extraction rate at 40°C, for different NaCl concentration samples

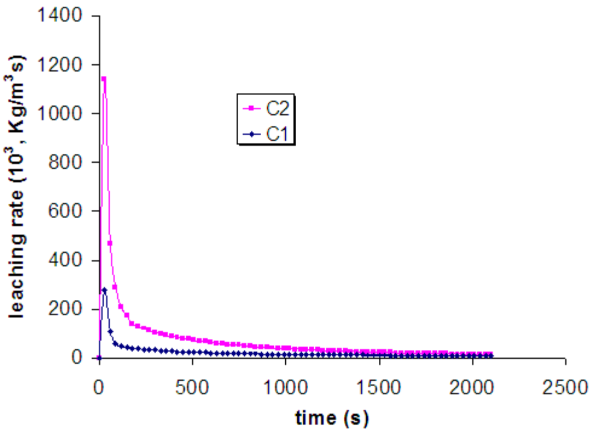

Fig. 15. The extraction rate, at a water flow rate of 13.3 L/h, at 30°C, at different $CaCl_2$ salt amounts of the samples

3.7. Extraction assessment based on mass transfer coefficient

The extraction process can be assessed by comparing the mass transfer coefficient values, namely the *k·a* products. It can be calculated using either the model applied to the current experimental data and proposed by the Eq. (6) or, directly, from the transferred salt flux from the solid particle to the liquid phase, according to the Eq. (9):

$$k \cdot a = \frac{\Delta m_{CaCl_2}}{\Delta t} \cdot \frac{1}{\Delta c_m} \qquad (9)$$

where:

$$\Delta c_m = C_{sat} - \sum c_i \qquad (10)$$

$$\Delta m_{CaCl_2} = M_v \Delta t \cdot \sum c_i - M_v \Delta t \cdot \sum c_{i-1} \qquad (11)$$

3.7.1. Mass transfer coefficient for a C₁=0.1334 CaCl₂ sample concentration, at 30°C

If the mathematical model given by the Eq. (6) is applied and plotted graphically, for the concentration variation in the time interval of 500-2100 seconds, a straight line is obtained. The slopes of the regression lines, for different flow rates, yielded a quantitative assessment of the mass transfer coefficients, namely the $k \cdot a$. The $k \cdot a$ product can be also obtained as a ratio between the $CaCl_2$ extracted quantity in a short period of time (30 s) and the average variation of $CaCl_2$ quantity in the sample, at a certain temperature. These values are given in Table 1 and plotted in Fig. 17, for the time interval of 210-2100 seconds, at 30°C.

It was found that the $k \cdot a$ product values fall within $2.7 \cdot 10^{-4}$ - $7.7 \cdot 10^{-6}$ s^{-1} range. The $k \cdot a$ value obtained according to the mathematical model (according to the Eq. 6) falls within this range. Note that this value is an average of the calculated $k \cdot a$ values for the time intervals of 30 s.

The $k \cdot a$ values obtained when the Eq. (9) is applied are higher at small flow rates, however they increase, at all three temperatures, according to the influence exerted by the convective diffusion and the liquid quantity that runs through the sample bed.

In the second stage of the process, the fluid flow does not influence any longer the solute diffusion and as a result, at the end of the interval, the $k \cdot a$ values are close, no matter the liquid flow rate. From Table 1, it is observed that the $k \cdot a$ values calculated based on the Eq. (6), at high flow rates, are very close to the lower limit of the range obtained base on the Eq. (9). This is due to the influence exerted by the internal diffusion on the solute extraction.

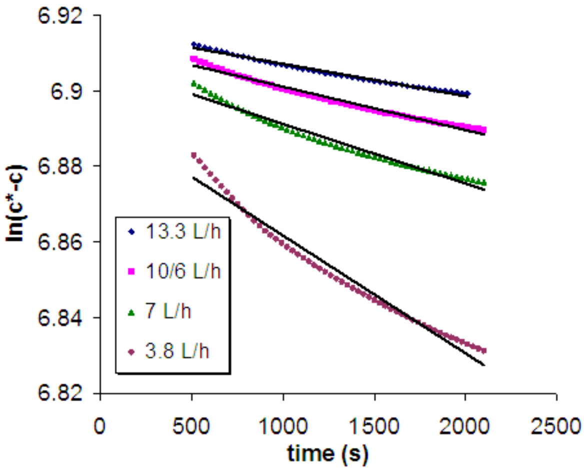

Fig. 16. Mass transfer coefficient at 30°C, small salt sample amount, different flow rates

Table 1. $k \cdot a$ product values for $CaCl_2$, calculated based on the experimental data

T(°C)	*M_v (L/h)*	*k·a (Eq. 6)(s^{-1})*	*Trendline equation (Eq. 6)*	*R^2*	*k·a (Eq. 9) (s^{-1})*
30°C	3.8	$3.11 \cdot 10^{-5}$	y = -3.11E-05x + 6.89	0.987	$6.0 \cdot 10^{-5}$ - $8.4 \cdot 10^{-6}$
	7	$1.58 \cdot 10^{-5}$	y = -1.58E-05x + 6.91	0.984	$1.4 \cdot 10^{-4}$ - $7.7 \cdot 10^{-6}$
	10.6	$1.15 \cdot 10^{-5}$	y = -1.15E-05x + 6.91	0.975	$2.1 \cdot 10^{-4}$ - $8.9 \cdot 10^{-6}$
	13.3	$0.852 \cdot 10^{-5}$	y = -8.52E-06x + 6.92	0.975	$2.7 \cdot 10^{-4}$ - $9.0 \cdot 10^{-6}$
20 °C	3.8	$3.75 \cdot 10^{-5}$	y = -3.75E-05x + 6.57	0.984	$4.3 \cdot 10^{-5}$ - $1.1 \cdot 10^{-5}$
	13.3	$1.2 \cdot 10^{-5}$	y = -1.20E-05x + 6.61	0.966	$1.4 \cdot 10^{-4}$ - $1.1 \cdot 10^{-5}$
40 °C	7	$1.25 \cdot 10^{-5}$	y = -1.25E-05x + 7.00	0.985	$1.6 \cdot 10^{-4}$ - $6.2 \cdot 10^{-6}$
	13.3	$7.56 \cdot 10^{-6}$	y = -7.56E-06x + 7.01	0.975	$1.8 \cdot 10^{-4}$ - $6.5 \cdot 10^{-6}$

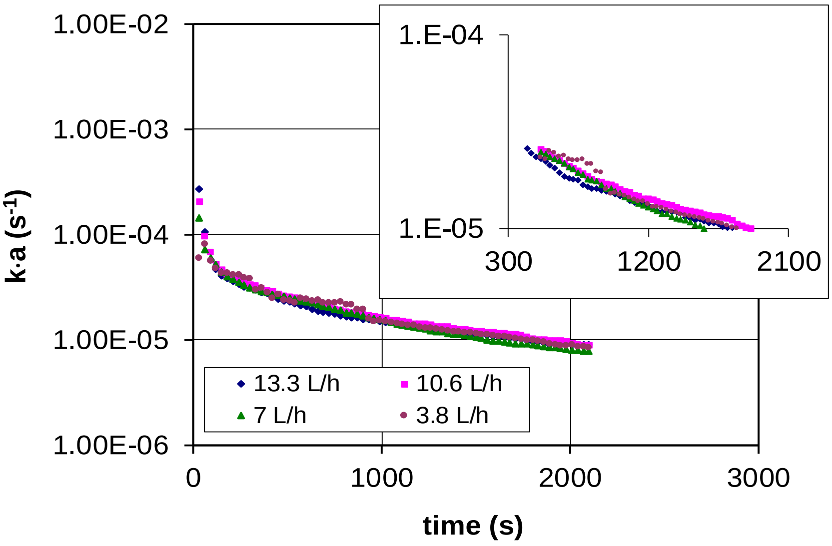

Fig. 17. Mass transfer coefficient $k \cdot a$ for $CaCl_2$ extraction, at 30°C, different liquid flow rates and small sample salt amount, C_1=0.1334

Table 2. *k·a* values for $CaCl_2$ calculated based on the experimental data

T (°C)	*M_v L/h)*	*k·a (Eq. 6)(s^{-1})*	*Trendline equation(Eq. 6)*	*R^2*	*k·a (Eq. 9)(s^{-1})*
20°C	3.8	$2·10^{-4}$	*y = -1.89E-04x + 6.14*	0.947	$6.5·10^{-4} ÷ 3.0·10^{-5}$
	7	$7.37·10^{-5}$	*y = -7.37E-05x + 6.39*	0.962	$1.0·10^{-3} ÷ 3.0·10^{-5}$
	10.6	$4.45·10^{-5}$	*y = -4.45E-05x + 6.50*	0.967	$1.6·10^{-3} ÷ 2.8·10^{-5}$
	13.3	$3.21·10^{-5}$	*y = -3.21E-05x + 6.53*	0.963	$1.6·10^{-3} ÷ 2.4·10^{-5}$
30 °C	3.8	$6.86·10^{-5}$	*y = -6.86E-05x + 6.78*	0.962	$4.3·10^{-4} ÷ 1.5·10^{-5}$
	7	$4.16·10^{-5}$	*y = -4.16E-05x + 6.83*	0.960	$6.8·10^{-4} ÷ 1.7·10^{-5}$
	10.6	$2.73·10^{-5}$	*y = -2.73E-05x + 6.85*	0.949	$9.5·10^{-4} ÷ 1.5·10^{-5}$
	13.3	$1.90·10^{-5}$	*y = -1.90E-05x + 6.86*	0.967	$1.1·10^{-3} ÷ 1.6·10^{-5}$
40 °C	3.8	$6.62·10^{-5}$	*y = -6.62E-05x + 6.88*	0.960	$2.8·10^{-4} ÷ 1.6·10^{-5}$
	7	$3.43·10^{-5}$	*y = -3.43E-05x + 6.93*	0.954	$8.9·10^{-4} ÷ 1.3·10^{-5}$
	10.6	$3.16·10^{-5}$	*y = -3.16E-05x + 6.87*	0.944	$1.1·10^{-3} ÷ 1.7·10^{-5}$
	13.3	$2.13·10^{-5}$	*y = -2.13E-05x + 6.97*	0.954	$9.4·10^{-4} ÷ 1.6·10^{-5}$

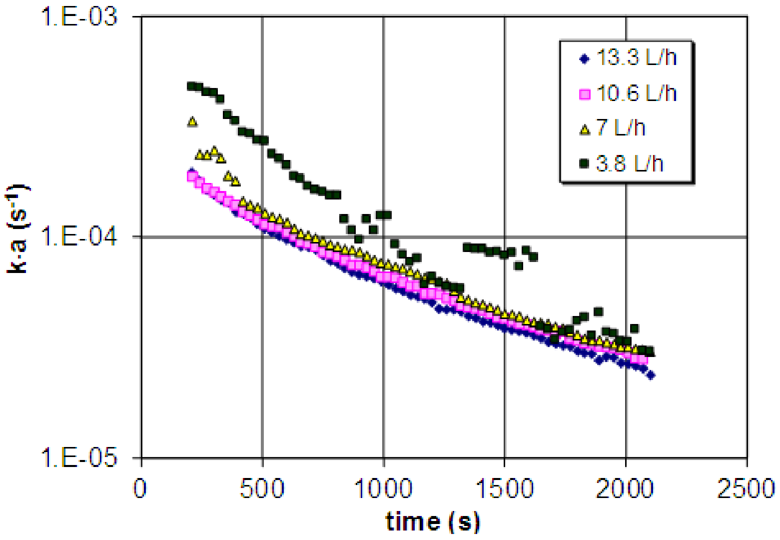

Fig. 18. *k·a* for $CaCl_2$ extraction, at 20°C, different liquid flow rates and large salt sample amount, C_2=0.2884

3.7.2. Mass transfer coefficient for a sample $CaCl_2$ concentration of C_2 =0.2884, at 20 °C

At 20°C and a $CaCl_2$ concentration of C_2 = 0.2884, at t>100 seconds, the mass transfer coefficient determined as the *k·a* product (Eq. 6), at different flow rates of 3.8 L/h, 7 L/h, 10.6 L/h, 13.3 L/h, takes values in the range of $2·10^{-4}$ - $7.37·10^{-5}$ s^{-1}. These values are consistent with those calculated for the *k·a* product using the Eq. (9), which gives values in the range of $1.6·10^{-3}$ - $3·10^{-5}$ (Fig. 18).

At the smallest flow rate (3.8 L/h), the *k·a* product has a much higher value than for the other three flow rates. At higher flow rates, the mass transfer coefficient values are quite close. For temperatures of 30°C and 40°C and t<1200 seconds, the *k·a* product values are dispersed. Looking at the data presented in Table 2, one can observe that the *k·a* values, obtained using the Eq. (9), are almost similar for the same temperature, with a maximum value at 20°C.

3.7.3. Mass transfer coefficient for different initial sample salt concentrations

According to the results in Fig. 8, (at point C, where an increase of the extraction rate due to an increase of the sample initial $CaCl_2$ amount was presented), the values for the *k·a* product, shown in Fig. 19, indicate also an intensification in the mass transfer with an increase in the sample salt concentration.

The *k·a* product, at a liquid flow rate of 13.3 L/h and 30°C, increases by 7.46 times at t = 210 seconds and only by 1.69 times at t = 2100 s, the decrease being due to the increased internal diffusion contribution to the extraction process. An increase by 1.73 times of the sample NaCl amount leads to an increase by 1.5 - 1.7 times of the mass transfer coefficient, at the same values of the liquid flow rate, temperature and time.

3.7.4. Influence of temperature on mass transfer coefficient

At the same liquid flowrate, the *k·a* product increases with the temperature decrease. The increase is larger at higher extraction time periods, as presented in Fig. 21, which is due to the internal diffusion influence.

For NaCl samples, in the first stage (t < 500 s), a higher temperature causes a higher mass transfer coefficient, afterwards its values decrease, as seen in Fig. 22. The temperature influence is particularly clear at time values greater than 700 s.

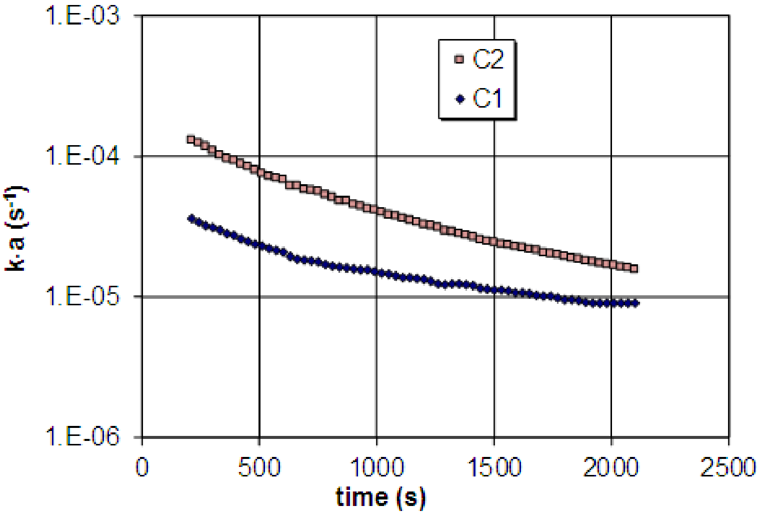

Fig. 19. Mass transfer coefficient, *k·a*, for CaCl$_2$, at 30°C, 13.3 L/h liquid flow rate, different sample salt concentrations

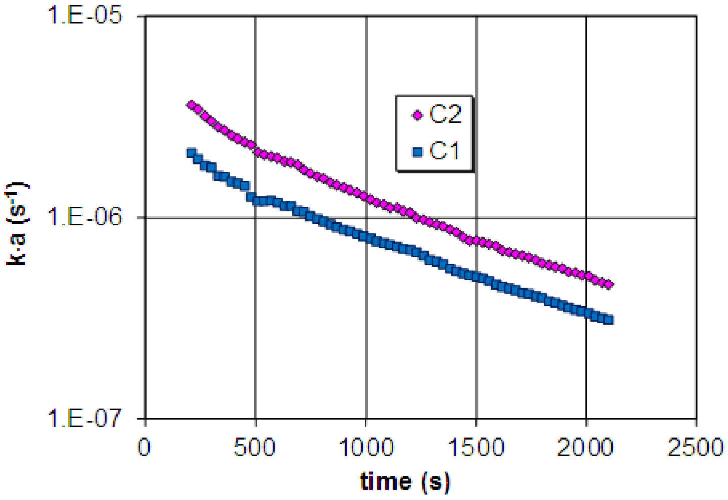

Fig. 20. Mass transfer coefficient, *k·a*, for different sample NaCl concentrations, at 40°C, 13.3 L/h liquid flow rate

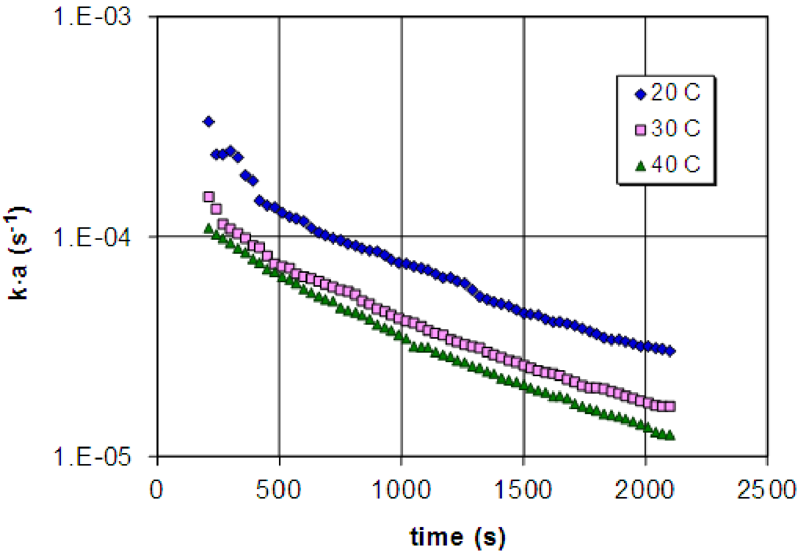

Fig. 21. Mass transfer coefficient, *k·a*, for large CaCl$_2$ sample amount, at different temperatures, 7 L/h liquid flow rate

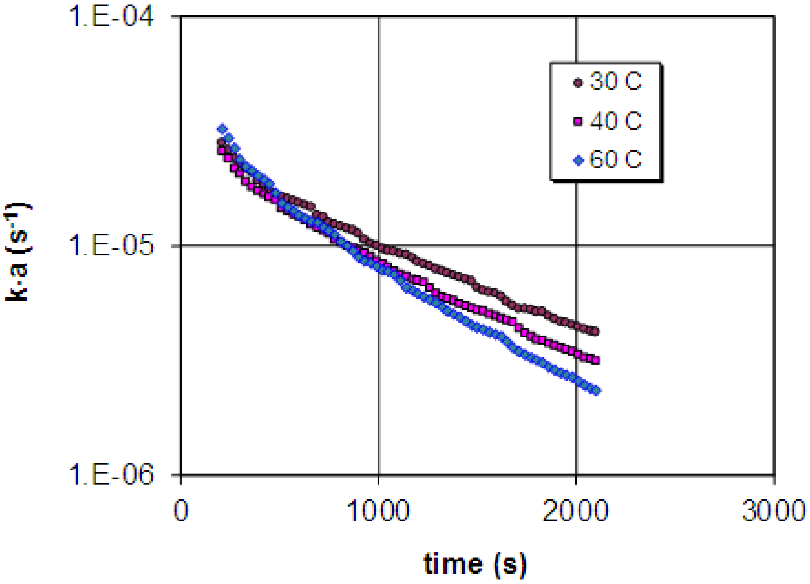

Fig. 22. Mass transfer coefficient, *k·a*, for sample large NaCl amounts, at different temperatures, 7 L/h flow rate

4. Conclusions

The solid-liquid extraction is a complex process, influenced by many factors. Our studies have shown that the liquid flow rate, sample solute amount and temperature are the key factors which determine a particular solute to be obtained. An optimum temperature for the extraction process has been recorded, which could be determined by the decrease of the solid-liquid contact time, although a temperature increase intensifies the diffusion.

The mass transfer coefficient value is difficult to obtain because it is not easy to appreciate the liquid phase - solid granules contact surface. That is why this was estimated by the *k·a* product, obtained using a mathematical model. The *k·a* product has been calculated, on one hand, as the average value for the time interval when the extraction is determined by the internal diffusion. On the other hand, the same *k·a* product was calculated for small time intervals, these values being determined by the temperature and the sample initial salt amount.

The used flow rate value in the extraction has an insignificant influence, the process being determined by the internal diffusion.

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