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Kinetics of uranium sorption onto weakly basic anion exchangers

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Abstract

Two weakly basic anion exchangers were investigated with respect to the kinetics of uranium sorption from drinking water. For theoretical description the combined film-particle diffusion model was applied. The two essential parameters in this approach, the liquid mass transfer coefficient β_L as well as the solid-phase diffusion coefficient D_s were determined from experiments and from comparison of experimental data and theoretical developments. Liquid-phase mass transfer coefficients were found to be in the order of magnitude of $\beta_L = 10^{-5}$ m/s, diffusion coefficients in the exchanger phases amounted to the range of $D_s = 10^{-12}$ m²/s for the acrylic exchanger Amberlite IRA 67 and $D_s = 10^{-13}$ m²/s for the polystyrene resin Lewatit MP 62. Because of the trace concentration level of Uranium species both steps affect the overall rate of sorption and none of them can be neglected.

Keywords: Sorption equilibrium; Sorption kinetics; Uranium; Weakly basic anion exchangers

1. Introduction

Uranium is a natural element and can be found in soils and rocks. In contact with water, it can be mobilised and, therefore, is found in many groundwaters as a trace component. Concentrations amount to up to 1 mg/L [1]. As a consequence, drinking water sources may be contaminated and uranium has to be eliminated prior to use. Naturally occurring uranium has very low levels of radioactivity. Its danger for human health mostly results from its properties as a heavy metal. Uranium usually is fast eliminated from the human body, however small amounts reach the blood stream. Studies show that elevated levels of uranium in drinking water can particularly affect the kidneys [1, 2]. There are still no standards for drinking water, there are, however, recommendations issued by e.g. WHO and the German Federal Environmental Agency (UBA) which range from 9-15 µg/L for lifelong consumption [1, 3].

In nature uranium is found in the oxidation states varying from +2 to +6. Calculations of the speciation of uranium for neutral or slightly alkaline CO_2-bearing water indicate that the very stable divalent and tetravalent uranyl carbonate ions $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ are predominant. In the presence of calcium ions, non-charged species $Ca_2UO_2(CO_3)_3$ may be predominant.

Ion exchange offers the possibility of selective sorption of uranium species. Especially at trace concentration levels it is, therefore, the method of choice for removal. Different kinds of processes have been proposed in literature. Most of them use strongly basic exchangers either in the chloride or in the sulphate form, respectively [4, 5, 6].

Weakly basic exchangers have successfully been tested for removal of traces of different heavy metals present as cations or oxy-anions [7]. At neutral pH values the amino groups of weakly basic exchangers with acrylic or acryl amide matrix are sufficiently protonated to allow a sorption of uranium-bearing species. Sorption can be described as:

$$\overline{2\cdot R_3-NH^+OH^-}+UO_2\left(CO_3\right)_2^{2-}\rightarrow\overline{\left(R_3-NH^+\right)_2UO_2\left(CO_3\right)_2^{2-}}+2\cdot OH^- \qquad (1)$$

(Overbarred quantities refer to species in the resin phase. In case of the exchange of a tetravalent anion four hydroxide ions are exchanged by one uranyl anion). The advantage of the application of weakly basic anion exchangers lies in the fact that they are very selective for metal species and that there is almost no exchange for ions from the background composition. As a result, there is practically no change of background composition of the water. Based on these properties, the process has been proposed for elimination of uranium trace impurities from contaminated ground waters and has been tested in the laboratory and pilot scales [8]. For technical application and for the design of full scale treatment plants it is essential to estimate and predict the performance of the respective filter columns which depends on the equilibrium and kinetics of sorption of uranium species. The investigation of these phenomena has, therefore, been the objective of work of this paper.

2. Materials and Methods

2.1. Exchangers

For the experiments the polystyrene-DVB-based anion exchanger Lewatit MP 62 and the acrylic weak base resin Amberlite IRA 67 were applied. MP 62 contains tertiary amine groups, it is practically mono-functional and characterized by low basicity and high stability. Amberlite IRA 67 has an acrylic backbone and possesses tertiary and secondary amine groups. The typical data of both exchangers are summarized in Table 1.

Table 1: Manufacturer data about the exchangers [9, 10]

			Lewatit MP 62	Amberlite IRA 67
Matrix			Styrene divinylbenzene copolymer	Acrylic divinylbenzene copolymer
Functional groups			Tertiary amine	Tertiary and secondary amine
Bead size		mm	0.3 – 1.25	0.3 – 1.0
Effective size	d_P	mm	0.47	0.5 – 0.75
Particle density	ρ_P	g/mL	1.02	n. d.
Particle density ^{exp}	ρ_P	g/mL	1.03	1.06
Bulk density ^{exp}	ρ_b	g/mL	0.65	0.68
Bulk porosity ^{exp}	ε	-	0.37	0.36
Total capacity		eq/L	1.7	1.6
Stability of temperature range		°C	1-100	60
Operating pH range		-	0 – 8	0 – 7
Shipping weight (dry bulk density)		g/mL	0.67	0.72

^{exp}: experimentally determined by authors

The resins were preconditioned by repeated treatment with HCl and NaOH solutions to remove impurities. After pre-treatment fractions of particle diameters in the ranges of 0.5 – 0.7 mm and 0.7 – 0.9 mm were sieved out for investigation of kinetics. For equilibrium and kinetic experiments a certain amount of the resin material was centrifuged for 20 min with 1280 fold of g to strip off water adhering at the surface of the beads. The quantities required for each individual experiment were weighed from this material.

2.2 Experimental Methods

Sorption equilibria were determined by equilibrating a series of samples of ion exchanger material (e.g. 0.1, 0.2, 0.4, 0.6, 0.8, 1g) with 4000 mL of uranium-bearing solution made of tab water. pH was adjusted by means of an imidazole buffer. The samples were shaken for 60 h at room temperature. After equilibration the pH values were measured and samples were taken from each vessel for analysis of uranium. Equilibrium loadings were calculated from the difference of initial and final concentrations.

Kinetic experiments were carried out by means of two different experimental setups. The first one was a basket stirrer apparatus as it has frequently been applied to studies of ion exchange kinetics [11, 12]. Figure 1 shows the scheme of the experimental setup, where the dashed area symbolises the layer of exchanger particles.

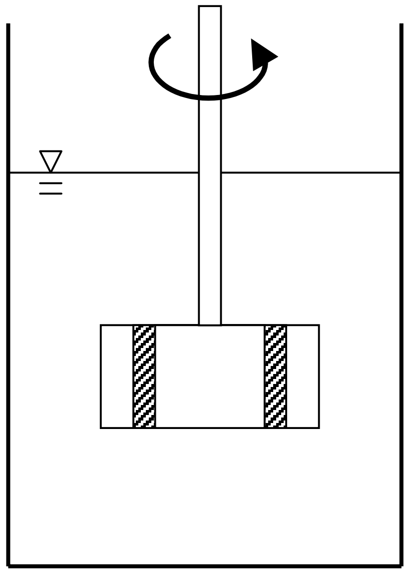


Figure 1: Scheme of the basket stirrer setup

The liquid phase consisted of 2.5 L of an uranium-bearing aqueous solution with initial concentrations of 1000 µg/L and 10 mMol/L imidazole buffer for adjusting pH. The basket stirrer contained 0.4 g of ion exchanger (weighed after centrifugation). The stirrer rotated in the solution at 150 1/min. Because of the stirring carbon dioxide was outgased and the pH increased. For counteracting carbon dioxide was aerated intermittently. All experiments were carried out at 20 °C. Samples of 5 ml were taken at preset time intervals to follow the sorption of uranium species. Uranium concentrations were measured by means of ICP-MS.

In technical filter columns the filter velocity (related to the free cross section) usually lies between 5 and 20 m/h. In the basket stirrer apparatus presented at the given rotation rate the flow velocity of the liquid passing the solid grains is up to 50 times higher [12]. Due to the large superficial velocity of the liquid phase the influence of film diffusion is reduced and the experimental setup thus allows studies of particle diffusion.

For investigations of film diffusion a short fixed bed column apparatus was applied as schematically shown in Fig. 2 [13]. A short packed bed is located between two layers of glass beads. The liquid phase passes the bed at constant flow rates which correspond to those of real filters. As with the basket stirrer, samples were taken from the column effluent to follow the development of exchange.

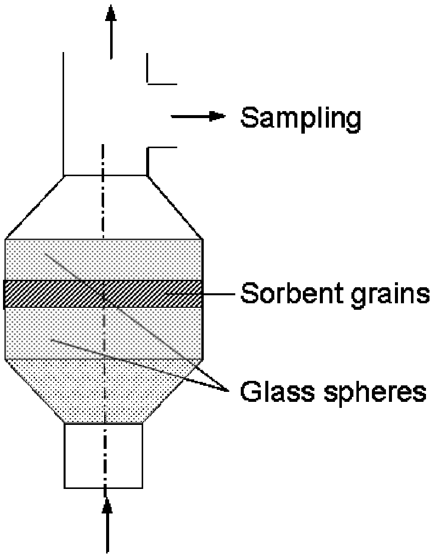


Figure 2: Short fixed bed setup

3. Theoretical description

3.1 Sorption equilibrium

Ion exchange equilibria can be correlated by means of numerical quantities (selectivity coefficients, distribution coefficients and separation factors) or by means of semi-empirical or empirical approaches as the usual Langmuir and Freundlich relationships.

$$q = q_{\max} \frac{K_L \cdot c}{1 + K_L \cdot c} \tag{2}$$

$$q = K_F \cdot c^n \tag{3}$$

The respective equilibrium parameters can be deduced from linearised plots or from nonlinear least square fitting of experimental data [14]. Here the latter method was selected.

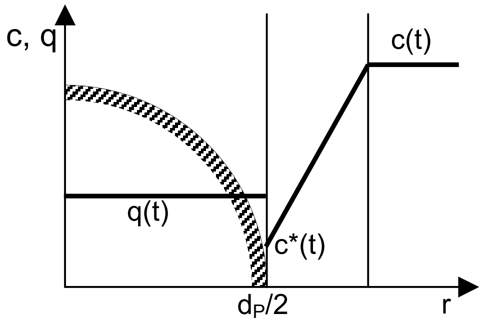
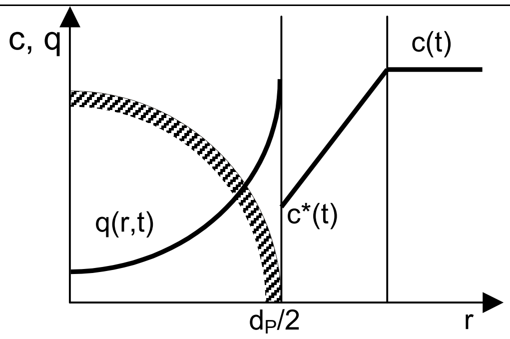
3.2 Sorption kinetics

The kinetics of ion exchange has widely been investigated and presented in a manifold of papers. Approaches for description can be based either on simple models like Fick's law approaches or on more sophisticated ones like the Nernst-Planck approach. Summaries are given in textbooks [14, 15]. As has been shown by Helfferich and co-workers the Nernst-Planck equations present the most accurate approach to describe ionic flux in ion exchange kinetics while Fick's law models can be applied for isotopic exchange and for exchange at trace concentration levels.

Corresponding to the speciation of uranium in the respective water the sorption develops as an exchange of a variety of U-bearing species for hydroxyl ions. It is, therefore, not a binary exchange but a kind of multicomponent system. Because the individual diffusion coefficients are not known, and because of the small uranium concentrations, Fick's law models with constant effective diffusion coefficients were selected for description.

The approach to equilibrium is composed of two transport steps, the diffusion across the Nernst diffusion layer (“film”) and inside of the particle. Depending on the circumstances one of these diffusion steps could become rate controlling. Film-diffusion control is often encountered in the case of small particle size, high concentration of fixed ionic groups, and diluted solutions. At contrary conditions, the development of exchange is controlled by particle diffusion [16, 17, 18, 19]. In intermediate cases, both the film diffusion and the particle diffusion affect the exchange. This case can mathematically be described by the combined film and particle diffusion model. The respective mathematical relationships for pure film diffusion and combined film-particle diffusion are summarised in Table 2 [14, 15].

Table 2: Mathematical relationships for description of film and particle diffusion in a batch reactor system

	Film diffusion	**Combined film-particle diffusion**
Model		
Mass transfer	$\frac{\partial c(t)}{\partial t}=\frac{6\cdot\beta_L\cdot m}{\rho_P\cdot d_P\cdot V}\left(c(t)-c^*(t)\right)$ (4a)	$\frac{\partial q(t,r)}{\partial t}=D_s\left(\frac{\partial^2 q(t,r)}{\partial^2 r}+\frac{2}{r}\frac{\partial q(t,r)}{\partial r}\right)$ (4b)
Mass balance	$c(t)+\frac{m\cdot q(t)}{V}=c_0$ (5a)	$c(t)+\frac{m\cdot \overline{q}(t)}{V}=c_0$ (5b)
Average particle loading	$\overline{q}=q(r=d_P/2)$ (6a)	$\overline{q}(t)=\frac{3}{\left(\frac{d_P}{2}\right)^2}\int_0^{d_P/2} q(t,r)r^2dr$ (6b)
Initial condition	$c(0)=c_0$ (7a) $q(0,r)=0$; for any r, $0\le r\le\frac{d_P}{2}$ (8a)	$c(0)=c_0$ (7b) $q(0,r)=0$; for any r, $0\le r\le\frac{d_P}{2}$ (8b)
Boundary conditions r = 0	- -	$\frac{\partial q(t,r=0)}{\partial r}=0$ (9b)
r = $d_P/2$	- -	$\frac{\partial q(t,r=d_P/2)}{\partial r}=\frac{\beta_L}{D_s\rho_P}\left(c(t)-c^*(t)\right)$ (10b)
Equilibrium at surface	$q(r=d_P/2)=f(c^*)=f(c(r=d_P/2))$ (11a)	$q(r=d_P/2)=f(c^*)=f(c(r=d_P/2))$ (11b)

Film diffusion mass transfer coefficients β_L can also be calculated by means of empirical relationships which, in general, have the form

$$Sh = f(\mathrm{Re}, Sc) \qquad (12)$$

with the dimensionless quantities Sherwood $\left(Sh = \beta_L \cdot d_P / D_L \right)$, Reynolds $\left(\mathrm{Re} = v_F \cdot d_P / \varepsilon \cdot \nu \right)$, and Schmidt $\left(Sc = \nu / D_L \right)$ numbers. The approaches used here are given in Table 3. For the respective relationships the liquid phase diffusion coefficient D_L of uranium species was calculated by means of a correlation developed by Worch [20]:

$$D_L = 3{,}595 \cdot 10^{-14} \frac{T}{\eta \cdot M^{0,53}} \qquad (13)$$

Table 3: Correlations to calculate the liquid phase mass transfer coefficient β_L

Wilson et al. [21]	$Sh = 1{,}09 \cdot \varepsilon^{-2/3} \mathrm{Re}^{1/3} Sc^{1/3}$ (14)	$0.0016 < \varepsilon \cdot \mathrm{Re} < 55$ $950 < Sc < 70000$
Kataoka et al. [22]	$Sh = 1{,}85 \cdot \left(\frac{1-\varepsilon}{\varepsilon} \right)^{1/3} \mathrm{Re}^{1/3} Sc^{1/3}$ (15)	$\mathrm{Re} \frac{\varepsilon}{1-\varepsilon} < 100$
Dwivedi et al. [23]	$Sh = \frac{1}{\varepsilon} \left(0.765 \cdot (\varepsilon \cdot \mathrm{Re})^{0.18} + 0.365 \cdot (\varepsilon \cdot \mathrm{Re})^{0.614} \right) \cdot Sc^{1/3}$ (16)	$0.01 < \mathrm{Re} < 15000$
Gnielinski [24]	$Sh = \left(2 + \sqrt{Sh_{lam}^2 + Sh_{tur}^2} \right) \left(1 + 1.5 \cdot (1-\varepsilon) \right)$ (17a) $Sh_{lam} = 0.644 \cdot \mathrm{Re}^{1/2} Sc^{1/3}$ (17b) $Sh_{tur} = \frac{0.037 \cdot \mathrm{Re}^{0.8} Sc}{1 + 2.443 \cdot \mathrm{Re}^{-0.1} \left(Sc^{2/3} - 1 \right)}$ (17c)	$\mathrm{Re} \cdot Sc > 500$ $Sc < 12000$

To obtain numerical solutions, the systems of equations were implemented in a computer program written in C++ language using finite-difference methods and both explicit and implicit calculation schemes. The Newton-Raphson method, dichotomy and the sweep method were used for a numerical solution of the sets of equations. The sweep method was applied to calculate the loading distribution inside the particles. The Newton-Raphson method was used to define both concentration and loading related to the particle surface. If the numerical solution at the next calculation step was outside of the reasonable range, a correct solution was found by means of the dichotomy (bisection) method [25, 26].

4. Results

4. 1. Sorption equilibrium

Figure 3 shows the resin loadings with uranium of both the acrylic resin Amberlite IRA 67 and the polystyrene exchanger Lewatit MP 62. Both exchangers show a dependency on pH, the weaker basic exchanger MP 62 even demonstrates a stronger one. This is due to strong increase/decrease of the share of protonated amino groups in this pH range. For IRA 67 there is obviously less influence of pH in the investigated range of 7.0 to 7.8.

Evaluation of equilibria was made by means of the Langmuir and Freundlich approaches. The resulting equilibrium constants are listed in Table 4.

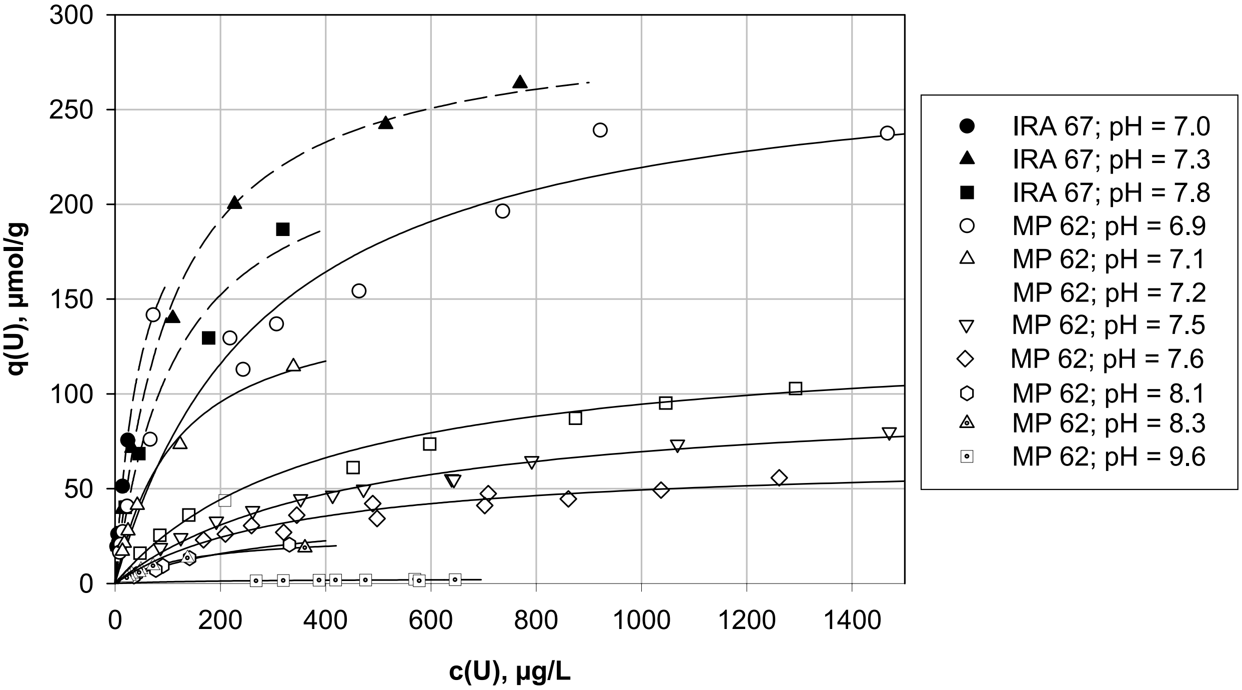


Figure 3: Isotherms of the sorption of uranium species onto Amberlite IRA 67 and Lewatit MP 62. Matrix: tap water, $c(U)_0$ = 1000/2000 µg/L. Lines: Langmuir isotherms.

Table 4: Equilibrium parameters

Resin	pH	Langmuir approach		Freundlich approach	
		q_{max} [µmol/L]	K_L [L/mg]	K_F [µmol L^n / g $µg^n$[WH1][WH2]]	n [-]
Lewatit MP 62	6.9	283	3.5	11.58	0.43
	7.1	152	8.5	5.28	0.53
	7.2	132	2.5	3.09	0.49
	7.5	101	2.2	2.76	0.47
	7.6	66	2.9	3.05	0.40
	8.1	40	3.3	0.42	0.67
	8.3	27	7.0	0.81	0.54
	9.6	2.5	5.1	0.26	0.31
Amberlite IRA 67	7.0	238	20.0	9.85	0.62
	7.3	296	9.2	17.94	0.41
	7.8	242	8.4	7.50	0.56

4.2. Film diffusion kinetics

Film diffusion was investigated by means of the short fixed bed system. As has been shown constant effluent concentrations are found as long as film diffusion is rate-controlling [14]. The level of effluent concentration depends on the flow velocity and increases with increasing velocity, i.e. with shorter contact time. From the effluent concentration the effective mass transfer coefficient β_L can be derived from the development of the approximately constant effluent concentration at the beginning of the column experiment [14]:

$$\beta_L\Big|_{t\to 0} = -\frac{\dot{V}}{m\cdot a_s}\ln\frac{c}{c_0} \qquad (18)$$

Mass transfer coefficients have been determined for empty bed filter velocities of 2, 5, 10, and 20 m/h. Determination was started at a high flow rate, after taking several samples a smaller velocity was adjusted. Further samples were taken before again decreasing the flow velocity. By this means a series of mass transfer coefficients was determined from one single experiment.

Results of one of these experiments with the exchanger Lewatit MP 62 are shown in Figure 4 which presents the standardised effluent concentrations c/c_0 as a function of time. The constant mean value of the standardised concentration was used to calculate the mass transfer coefficient $ß_L$. The mass transfer in the liquid only depends on the hydrodynamic conditions and the particle size. Therefore, analogous experiments with Amberlite IRA 67 led to identical results.

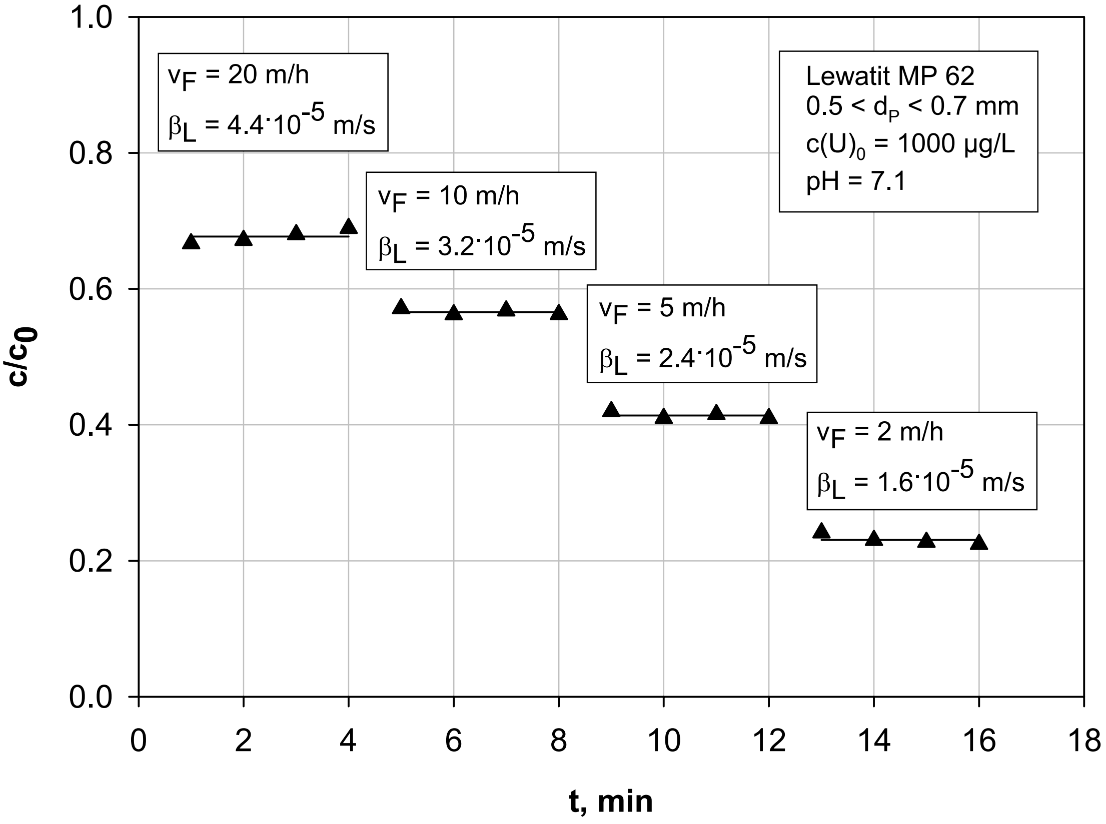


Figure 4: Standardised filter effluent concentrations for determination of mass transfer coefficients, $m = 2.5$ g, $A_F = 4.9$ cm², $a_s = 9.8$ m²/kg

The development of experimentally obtained mass transfer coefficients β_L (for a particle diameter of 0.6 mm) and values calculated from empirical relationships as a function of the filter velocity v_F are plotted in Figure 5. The results show that the experimental data are more or less well predicted by the empirical relationships.

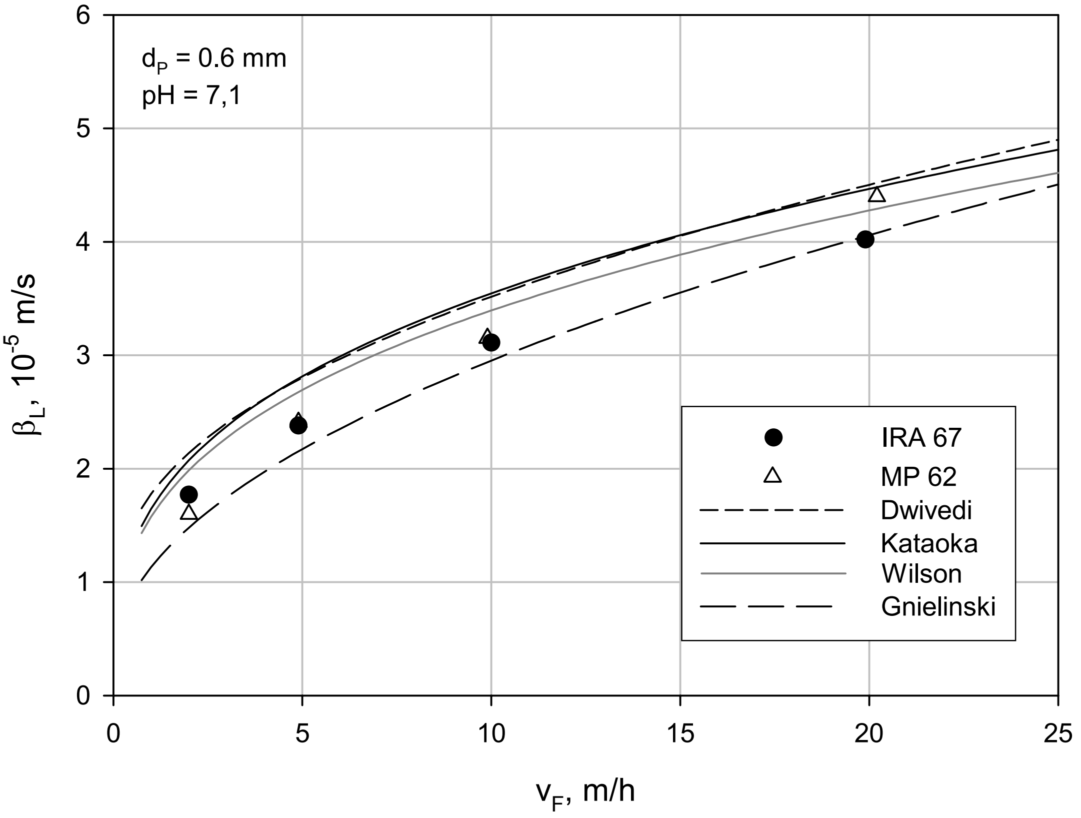


Figure 5: Experimental detected and calculated values for mass transfer coefficient in dependence of the filter velocity, d_P = 0.6 mm, pH = 7.1.
Calculation input: Uranium complex: $UO_2(CO_3)_2^{2-}$ (M = 390 g/mol), d_P = 0.6 mm, ε = 0.37, T = 293.15 K

During determination of the mass transfer coefficients with the sieved fraction with an average diameter of d_P = 0.8 mm the pH value was slightly shifted to a higher value of 7.5 (Figure 6). Here a strong influence of pH was detected. At a pH value of 7.5 the speciation of Uranium changes (towards the tetravalent uranyl tri-carbonate complex) and the mass transfer coefficient increases considerably. As a consequence, the mass transfer coefficient could no longer be described by the approaches presented above.

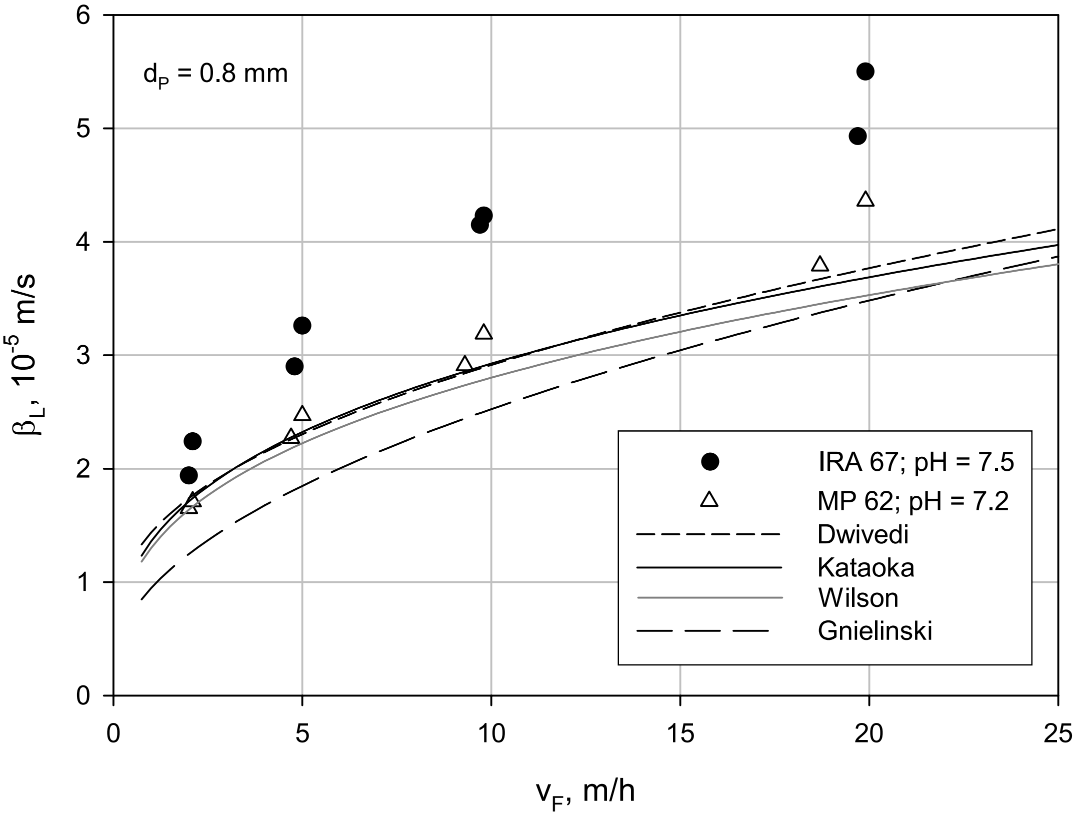


Figure 6: Experimental detected and calculated values for mass transfer coefficient in dependence of the filter velocity, d_P = 0.8 mm, pH = 7.2 / 7.5.

Calculation input: Uranium complex: $UO_2(CO_3)_2^{2-}$ (M = 390 g/mol), d_P = 0.8 mm, ε = 0.37, T = 293.15 K

4.3 Particle diffusion kinetics

Figure 7 shows the development of the liquid phase concentration and the corresponding pH values from a basket stirrer experiment performed with the resin Lewatit MP 62. Furthermore, the figure contains theoretical developments calculated under the assumptions of both, pure film and combined film-particle diffusion, respectively. The calculations were based on application of the Langmuir relationship for description of the equilibrium and fitted equilibrium constants at a pH value of 7.3. For film-particle diffusion calculations a film mass transfer coefficient of $\beta_L = 1.7 \cdot 10^{-4}$ m/s was assumed which was deduced from the slope of the development of the concentration of uranium species at the beginning of the experiment [14].

The development shows the influence of particle diffusion. Assuming pure film diffusion leads to a faster decrease of the liquid phase concentration than the combined film / particle diffusion. Calculation with different values of the effective particle diffusion coefficient yielded an optimum effective diffusion coefficient of $D_S = 2 \cdot 10^{-13}$ m²/s. As the developments show particle diffusion affects the equilibration only after an initial period. The comparison demonstrates that the assumption of a combined film and particle diffusion mechanism allows a very satisfactory description of sorption kinetics.

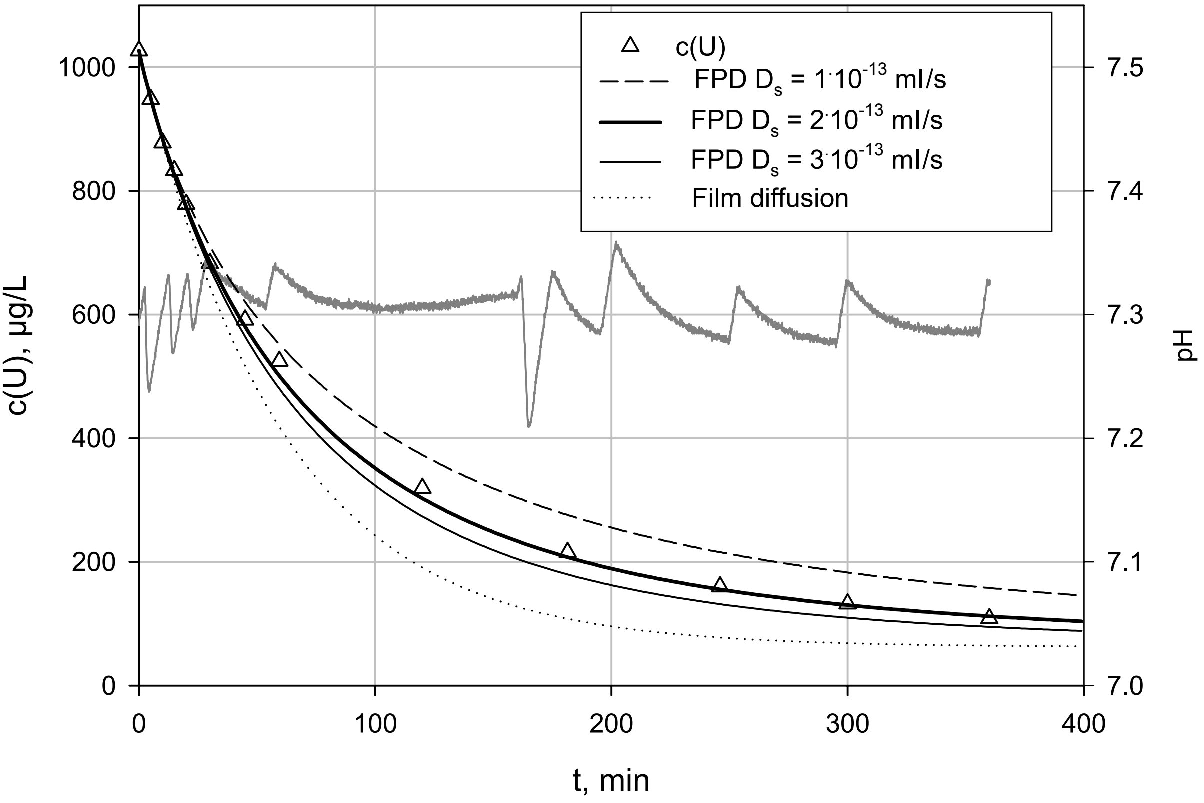


Figure 7: Development of concentration during a basket stirrer experiment and current pH-value. Exchanger: Lewatit MP 62, 0.5 – 0.7 mm, Solution: spiked tap water. Symbols: experimental results, lines: calculated developments. Film mass transfer coefficient: $1.7\cdot10^{-4}$ m/s

Evaluation of effective particle diffusion coefficients for resin material with the different particle size fractions yielded identical values for both resins (data are summarized in Table 5). However, much higher diffusion coefficients in the range of 10^{-12} m²/s were found for the acrylic exchanger Amberlite IRA 67. Unfortunately, the determination of the effective particle diffusion coefficients of this exchanger is not very accurate at the chosen experimental conditions.

Table 5: Diffusion coefficients at different particle size

	D_s [m²/s]	
Particle diameter	$0.5 < d_P < 0.7$	$0.7 < d_P < 0.9$
Lewatit MP 62	$2\cdot10^{-13}$	$2\cdot10^{-13}$
Amberlite IRA 67	$1\cdot10^{-12}$	$1\cdot10^{-12}$

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List of symbols

A_F	m^2	Cross-sectional area of packed bed
a_s	m^2/kg	Specific outer surface
c	mol/L	Concentration
c_0	mol/L	Initial concentration
c^*	mol/L	Concentration at the particle surface
D_L	m^2/sec	Liquid phase diffusion coefficient
D_s	m^2/sec	Effective particle diffusion coefficient
d_P	m	Particle diameter
M	g/mol	Molar mass
m	g	Mass of sorbent
q(t, r)	g/g	Uranium loading
r	m	Radial coordinate (0<=r<=d/2)
T	K	Temperature
t	sec	Time
V	L	Volume of solution
$\dot{V}$	m^3/sec	Flow rate
v_F	m/sec	Filter velocity
β_L	m/sec	Liquid phase mass transfer coefficient
ε	-	Bulk porosity
η	$Pa \cdot sec$	Dynamic viscosity
ν	m^2/sec	Kinematic viscosity
ρ_b	g/L	Bulk density
ρ_P	g/L	Sorbent density

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