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Effective intraparticle diffusion coefficients of $CoCl_2$ in mesoporous functionalized silica adsorbents

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Abstract The scope of this work is to determine the effective intraparticle diffusion coefficient of $CoCl_2$ over mesoporous functionalized silica. Silica is selected as a carrier of the functionalized groups for its rigid structure which excludes troublesome swelling, often found in polymeric adsorbents. 2-(2-pyridyl)ethyl-functionalized silica is selected as a promising affinity adsorbent for the reversible adsorption of $CoCl_2$. The adsorption kinetics is investigated with the Zero Length Column (ZLC) method. Initially, experiments were performed at different flow rates to eliminate the effect of external mass transfer. The effect of pore size (60 Å and 90 Å), particle size ($40{\cdot}10^{-6}$ m–$1000{\cdot}10^{-6}$ m) and initial $CoCl_2$ concentration (1 mol/m^3–2.0 mol/m^3) on the mass transfer was investigated. A model was developed to determine the pore diffusion coefficient of $CoCl_2$ by fitting the experimental data to the model. The pore diffusion coefficients determined for two different pore sizes of silica are $D_p(60\ \text{Å}) = 1.95{\cdot}10^{-10}$ [m^2/s] and $D_p(90\ \text{Å}) = 5.8 \cdot 10^{-10}$ [m^2/s]. The particle size and the initial $CoCl_2$ concentration do not have an influence on the value of diffusion coefficient. However, particle size has an influence on the diffusion time constant. In comparison with polymer adsorbents, silica based adsorbents have higher values of diffusion coefficients, as well as a more uniform and stable pore structure.

Keywords Effective intraparticle diffusion coefficients · Mesoporous silica · ZLC method

Abbreviations

b	Langmuir adsorption constant, m^3/mol
C	Adsorbate concentration, mol/ m^3
C_0	Initial adsorbate concentration, mol/ m^3
C_e	Equilibrium adsorbate concentration, mol/ m^3
C_{NRM}	Adsorbate concentration with a non-recycle mode, mol/ m^3
C_{RM}	Adsorbate concentration with a recycle mode, mol/ m^3
C_{exp}	Experimental adsorbate concentration, mol/ m^3
D_a	Macropore diffusion coefficient, m^2/s
D_i	Micropore diffusion coefficient, m^2/s
D_p	Intraparticle diffusion coefficient, m^2/s
F	Volumetric flow, ml/min
K_i	Diffusion time constant, 1/s
m	Mass of adsorbent, kg
q	Loading of the adsorbent, mol/kg
$\bar{q}$	Averaged loading of the adsorbent, mol/kg
q_{exp}	Experimentally determined loading of the adsorbent, mol/kg
q_s	Maximal loading of the adsorbent, mol/kg
r	Radial position in the particle, m
R	Radius of the particle, m
ρ_s	Density of the solid, kg/m^3
t	Time, s
V	Volume of solution, m^3
V_{bed}	Volume of the bed in the ZLC set-up, m^3
V_{extra}	Volume of the ZLC set-up, m^3
V^*_{extra}	Volume of the ZLC set-up with empty bed, m^3

1 Introduction

Dunnewijk et al. (2004), proposed Reverse Flow Adsorption (RFA) as a novel concept for the recovery and recy-

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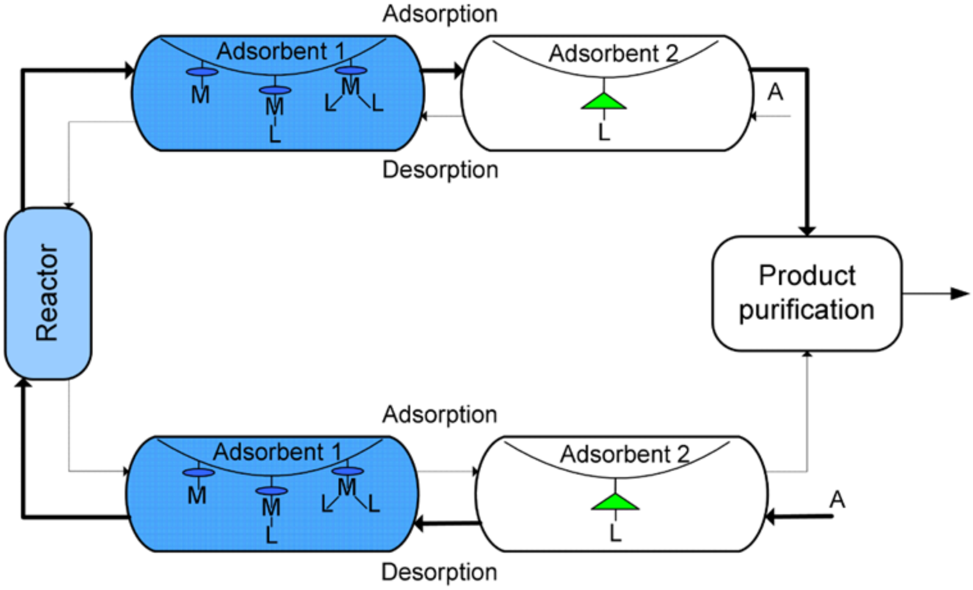

Fig. 1 Reverse flow adsorption (RFA) concept

cling of homogeneous catalysts (Fig. 1). They selected polymer adsorbents: Amberlyst A 21 and Polymerbound PPh_3 for adsorption of $CoCl_2$, and Ag^+ loaded Amberlyst 15 for adsorption of triphenylphosphine (Dunnewijk et al. 2005), whose mass transfer properties they studied (Dunnewijk et al. 2006). Amberlyst A 21 and Ag^+ loaded Amberlyst 15 are bi-dispersed particles consisted of the macro- and micropores, while polymerbound PPh_3 is mono-dispersed microporous polymer material. The major drawback of these adsorbents for application in the RFA concept appeared the swelling of the adsorbent and the presence of micropores that caused a high mass transfer resistance. The slow diffusion in the particles and unstable particle properties due to swelling require longer residence times to prevent leaching from the adsorption bed and consequently larger bed volumes (Dunnewijk 2006).

To overcome these limitations silica is selected as a carrier for different functionalized groups. A large surface area, a wide range of pore sizes and a stable structure make silica a potentially ideal carrier. Silica is widely used for adsorption purposes as non-functionalized adsorbent (Aristov et al. 2006), carrier for the immobilization of functional groups (Li et al. 2007), or as an already functionalized adsorbent (Qu et al. 2006). In our previous work (Djekić et al. 2007) a wide range of functionalized silica adsorbents was evaluated, and 2-(2-pyridyl)ethyl-functionalized silica was selected as a promising adsorbent for the reversible adsorption of cobalt (II) chloride. The goal of this chapter is to determine the effective intraparticle diffusion coefficients of cobalt (II) chloride inside the 2-(2-pyridyl)ethyl-functionalized silica by using the Zero Length Column (ZLC) method (Eic and Ruthven 1988; Brandani and Ruthven 1995; Dunnewijk et al. 2006) and compare these results with results obtained in a work of Dunnewijk et al. (2006). Comparison of these adsorbents, selection of the more suitable one and the determined effective intraparticle diffusion coefficients are essential for further development and design of the RFA concept for the recovery of homogeneous catalysts.

This paper starts first by describing the mathematical model that takes into account the intraparticle diffusion as the rate limiting step and is used to determine the effective intraparticle diffusion coefficients. Afterwards, the used materials and the ZLC set-up are discussed. To achieve our objectives ZLC experiments are performed at high flow rates to eliminate both external mass transfer and axial dispersion. The effective intraparticle diffusion coefficients are calculated from the experimental data by fitting the developed model to the experimental data to determine the effective diffusivity and to investigate the effects of pore size, particle size and concentration of the adsorbate. Temperature effect is excluded in this study, and its investigation will be performed in the continuation of the project. The paper is concluded with a comparison between polymeric adsorbents and silica adsorbents and final conclusions are drawn on the suitability of adsorbents.

2 Mathematical model

To determine the diffusion coefficient of the sorbate inside the particle several assumptions are made:

- 2-(2-pyridyl)ethyl-functionalized silica has a uniform pore size distribution.
- The length of the bed is sufficiently small that change of concentration in the axial direction can be neglected as well as axial dispersion.

- The flow of the sorbate is sufficiently high to neglect the film layer around the particle and therefore the external mass transfer resistance can be neglected.
- Due to mesopore silica structure contribution of surface diffusion is significantly smaller compared to intraparticle diffusion (Guiochon et al. 2006). However, both effects are lumped into one effective intraparticle diffusion coefficient.
- The equilibrium between the liquid and the solid phase is described by a Langmuir isotherm.

The mass balance of the adsorbate inside the particle is described by (1):

$$\varepsilon_p \frac{\partial C}{\partial t} + (1-\varepsilon_p)\rho_S \frac{\partial q}{\partial t} = \varepsilon_p \cdot D_p \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r} \right) \tag{1}$$

The Langmuir isotherm is described by (2):

$$q = \frac{C \cdot b \cdot q_s}{1 + C \cdot b} \tag{2}$$

The initial conditions are:

$$\text{For} \quad t = 0 \quad \text{and} \quad r = R: \quad C = C_0 \quad \text{and} \tag{3}$$

$$\text{For} \quad t = 0 \quad \text{and} \quad r < R: \quad C = 0 \tag{4}$$

The boundary conditions are:

$$\text{For} \quad t \neq 0 \quad \text{and} \quad r = R: \quad C = C(R) \tag{5}$$

and due to symmetry

$$\text{For} \quad t \neq 0 \quad \text{and} \quad r = 0: \quad \left(\frac{\partial C}{\partial r} \right) = 0 \tag{6}$$

Detailed explanation of each symbol is given in Abbreviations.

The concentration of the solute at the surface of the particle is assumed to be equal to the bulk concentration since the external mass transfer resistance is neglected. This concentration is given by the overall mass balance:

$$\frac{dC(R)}{dt} + \frac{m}{V}\frac{d\bar{q}}{dt} = 0 \tag{7}$$

$$\bar{q} = \frac{3}{R^3}\int_0^R r^2 \cdot q \cdot dr \tag{8}$$

The effective intraparticle diffusion coefficient is determined by fitting the model to the measured solute concentration profile over time. During fitting the following objective function is minimized:

$$\sum_{t=0}^{n} (C_{\text{exp}} - C(R))^2 \rightarrow \min \tag{9}$$

where n presents the total amount of time needed for the experiment. In parallel the diffusion time constant, K_i [1/s], is calculated as:

$$K_i = \frac{D_p}{R^2} \tag{10}$$

The calculations were performed with the software package MATLAB.

3 Materials

Cobalt(II)chloride (anhydrous) and acetonitrile (MeCN) (99.9%) were obtained from Sigma-Aldrich. 2-(2-pyridyl)-ethyl-functionalized silica was produced by Silicycle and obtained via Screening Devices. No preliminary treatment of acetonitrile or the silica adsorbent was performed. Three batches of silica were used and their properties are presented in Table 1. Batches 2 and 3 are sieved and three fractions are obtained as shown in Table 1.

4 Experimental

4.1 Adsorption equilibrium experiments

All adsorption equilibrium experiments were conducted according to the experimental procedure described in our previous work (Djekić et al. 2007).

4.2 ZLC set-up

The ZLC set-up was built to investigate the mass transfer properties necessary to determine the effective intraparticle diffusivity (see Fig. 2). The set-up consists of a pump (Knauer K-1001), an UV/Vis detector (Knauer K-2600), two

Table 1 Properties of functionalized silica

	Pore size [Å]	Intraparticle porosity [−]	Surface area [m^2/g]	Particle size [10^{-6} m]	Sieved fractions [10^{-6} m]		
					I	II	III
Batch 1	60	0.6	500	40–63	–	–	–
Batch 2	60	0.6	500	500–1000	500–700	700–810	810–1000
Batch 3	90	0.63	500	500–1000	500–700	700–810	810–1000

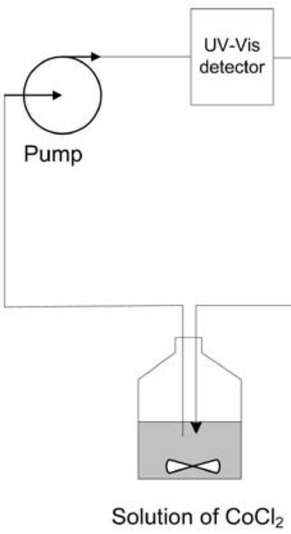

Fig. 2 Schematic representation of the ZLC set-up in recycle mode

heat exchangers (H.E. I and H.E. II), a column (Omnifit), an oven, two thermocouples and two vessels. The pump flows applied were 10, 20, 30, 40 and 50 ml/min. The UV/Vis detector was set at 656 nm to detect cobalt(II) chloride. Heat exchanger H.E. I was used to heat the flow to 30°C which was also the temperature of the oven in which the column was placed. Heat exchanger H.E. II was used to cool the liquid flow to the room temperature. This operating procedure assures that the measurements by the UV/Vis detector were not effected by temperature fluctuations. During the experimental work, the ZLC set-up was used in two modes: non-recycling and recycling. In the non-recycle mode the inlet and the outlet tubes are in two separate vessels. This mode is used for cleaning the set-up and reaching an equilibrium state. In the recycling mode the inlet and the outlet tube of the set-up are placed in the same vessel equipped with a stirrer to assure ideal mixing. This mode is used for all kinetic experiments. The internal column diameter was $15{\cdot}10^{-3}$ m, and the length of the bed was not exceeding $2{\cdot}10^{-3}$ m.

All kinetic experiments are performed according to the same procedure. First the column is loaded with $0.2{\cdot}10^{-3}$ kg of the 2-(2-pyridyl)ethyl-functionalized silica. Then the set-up is equilibrated with the pure solvent in the non recycle mode. Afterwards, the pure solvent is replaced with the $40{\cdot}10^{-6}$ m^3 of $CoCl_2$ solution and the set-up is changed to the recycle mode. The UV-Vis signal over time is monitored online and recorded by a PC. Fresh silica is used for each experiment. Regeneration of silica was avoided due to time consumption. Some experiments are repeated including all experimental steps and reproducibility appeared to be within 2.5%.

Extra volume of the ZLC set-up is determined according the procedure described in the work of Dunnewijk et al. (2005). The extra volume is determined for four different initial concentrations (0.5, 1, 1.5 and 2 [mol/m^3]) and the averaged extra volume, $V_{extra,}$ is calculated to be $3.48 \pm 0.06 \cdot 10^{-6}$ m^3.

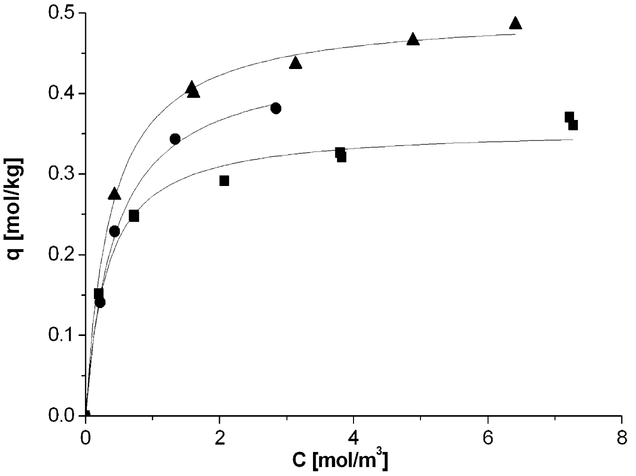

Fig. 3 Equilibrium isotherms of $CoCl_2$ on 2-(2-pyridyl)-functionalized silica for three different batches at 30 °C: *full squares* (■): Batch 1; *full circles* (●): Batch 2; *full triangles* (▲): Batch 3

Table 2 Coefficients of the Langmuir isotherms used to model the adsorption equilibrium of three different functionalized silica batches at 30 °C

	b [m^3/mol]	q_S [mol/kg]
Batch 1	3.20	0.357
Batch 2	2.28	0.447
Batch 3	2.68	0.501

5 Results and discussion

5.1 Adsorption isotherms

In this work we used three batches of 2-(2-pyridyl)ethyl-functionalized silica adsorbents. The number of active sites on each silica is different. Therefore the adsorption isotherm was measured and modelled by the Langmuir isotherm for each batch (Fig. 3). The coefficients of the Langmuir isotherm (2), b and q_S, are given in Table 2. As shown, the bonding strength, b, for each batch is the same within the experimental error and the fitting. This is expected since there is always the same interaction between the adsorbate, $CoCl_2$, and the pyridine group on the silica surface. However, the number of sites differs for each batch. To minimize error in the fitted diffusion coefficient for each batch the corresponding b and q_S values are used.

5.2 Influence of the liquid flow

The adsorption mass transfer is a function of the external and the internal mass transfer resistance. At sufficiently high flow rates contribution of the external mass transfer resistance can be neglected, and the change of concentration over time is determined only by intraparticle diffusion. Therefore, the first step was to monitor the change of the cobalt(II) chloride concentration over time as a function of the volumetric flow rate. Figure 4 shows the results for three batches: Batch 1, Batch 2/Fraction I and Batch 3/Fraction I. Since the external mass transfer is also inversely proportional to the particle size (Guiochon et al. 2006), the influence of the external mass transfer is best shown for Batch 1 since it contains the smallest particles. Figure 4a clearly shows that the difference between 40 and 50 ml/min is negligible. Since the maximum volumetric flow of the pump is 50 [ml/min], this flow rate was selected to determine the effective intraparticle diffusion coefficient for Batch 1. For both, Batch 2/Fraction I (Fig. 4b) and Batch 3/Fraction I (Fig. 4c), the influence of external mass transfer at flow rate of 40 ml/min is negligible. The fitted effective intraparticle diffusivity was based on these data. Fractions II and III of Batch 2 were also tested (see the influence of the particle size), and also in these experiments influence of the external mass transfer is not noticed for volumetric flows of 10 and 40 [ml/min].

5.3 Influence of the particle size

The influence of particle size on the internal mass transfer rate is shown by adsorbing cobalt(II)chloride on four different ranges of silica's particle sizes: 40–63, 500–710, 710–800 and 800–1000 [10^{-6} m]. Figure 5 shows both experimental and model results of the $CoCl_2$'s concentration change over time. Table 3 gives both the fitted pore diffusion coefficients and diffusion time constants for all four particle sizes. As expected particle size does not have any influence on the effective pore diffusion coefficient, in contrast to the diffusion time constant, K_i, used to describe the internal mass transfer rate. The smaller particle sizes are preferable since they increase the internal mass transfer rate. On the other hand, handling of the smaller particles, such as particles with 40–63 [10^{-6} m] diameter, will certainly lead to high pressure drops inside the adsorption columns. Therefore a balance between required pressure drop within an adsorption bed and mass transfer rate in a bed is needed.

5.4 Influence of the pore size

To investigate the effect of pore size on diffusivity two silica adsorbents with different pore sizes with a mean diameter of 60 Å and 90 Å (respectively Batch 2 and 3) are selected. Figure 6 shows experimental data and model results of $CoCl_2$ concentration change over time for the selected silica. Results clearly show the faster concentration change of $CoCl_2$ for a larger pore diameter. The results of the fitted effective intraparticle diffusion coefficients and the diffusion time constants are shown in Table 3. The difference in the effective intraparticle diffusion coefficients can be partially

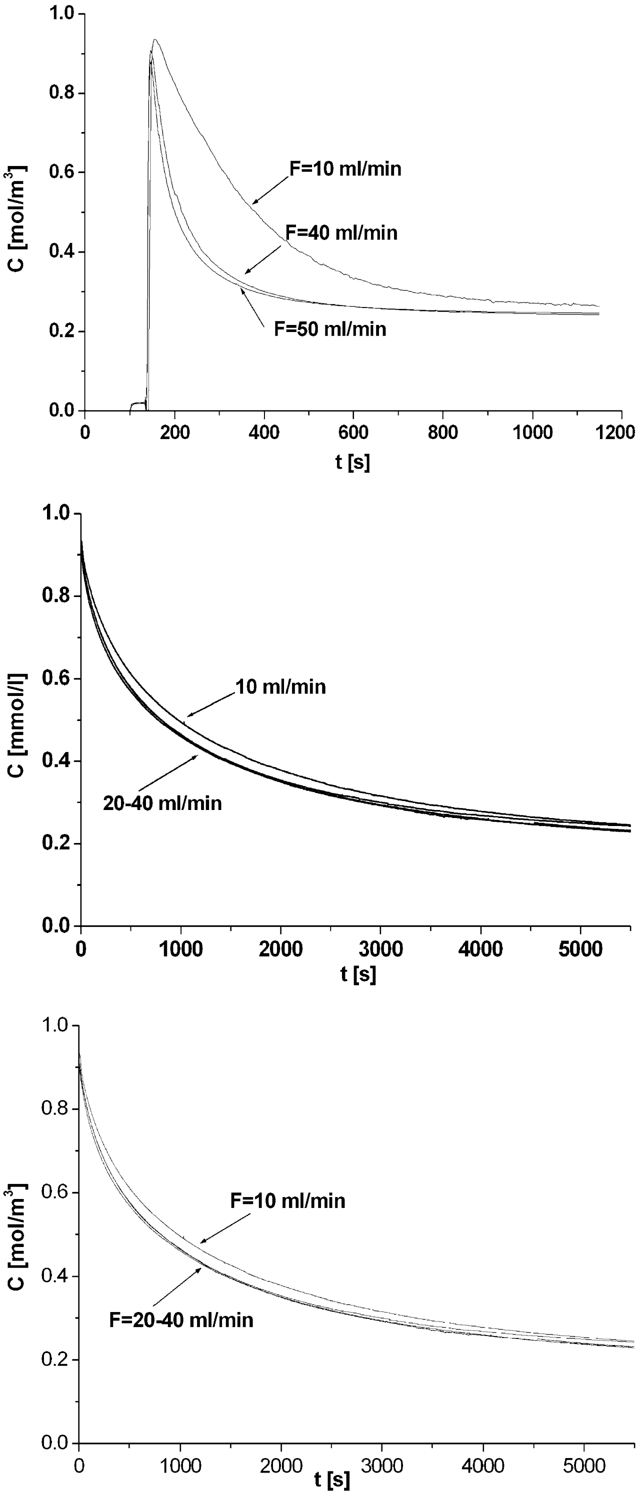

Fig. 4 Cobalt(II) chloride's concentration in the liquid phase as a function of time during adsorption at 30 °C on: (**a**) Batch 1, (**b**) Batch 2/Fraction I, (**c**) Batch 3/Fraction I at different volumetric flows

Table 3 The pore diffusion coefficient and the reciprocal time constants at 30 °C for four different particle sizes and two pore sizes

Batch	1		2		3
Pore size [Å]	60		60		90
Particle size [10^{-6} m]	40–63	500–710	710–800	800–1000	500–710
D_P [m^2/s]	$1.75\cdot10^{-10}$	$1.95\cdot10^{-10}$	$1.92\cdot10^{-10}$	$2.03\cdot10^{-10}$	$5.8\cdot10^{-10}$
K_i [1/s]	$2.63\cdot10^{-1}$	$2.13\cdot10^{-3}$	$1.35\cdot10^{-3}$	$1.03\cdot10^{-3}$	$6.34\cdot10^{-3}$

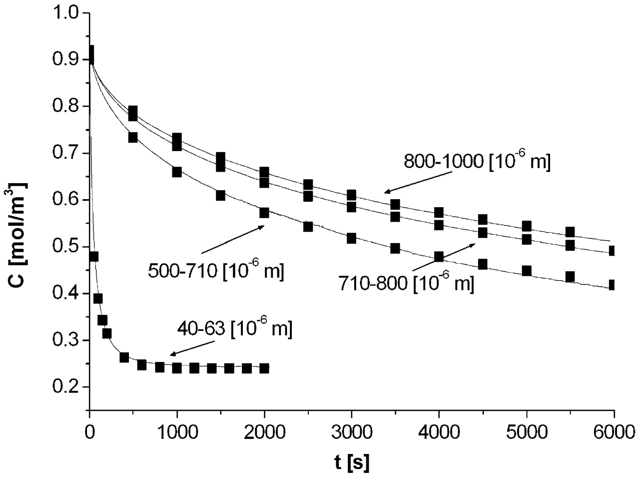

Fig. 5 The experimental (*solid line*) and the model (*full square*) results of $CoCl_2$'s concentration changes over time during its adsorption on four different particle ranges of 2-(2-pyridyl)-functionalized silica at 30 °C

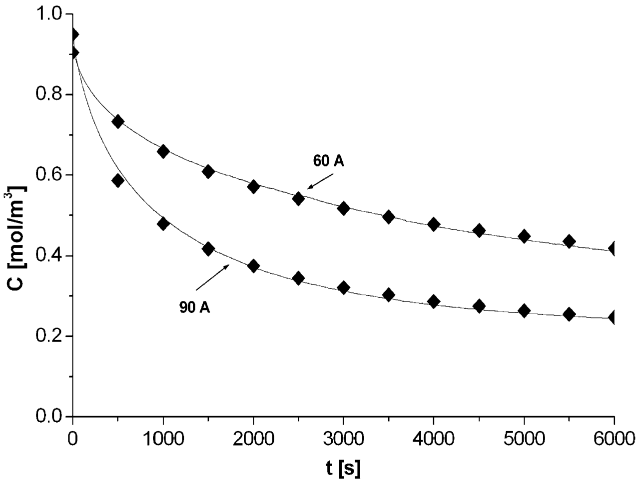

Fig. 6 The experimental (*solid line*) and the model (*full diamonds*) results of the $CoCl_2$ concentration change over time at 30 °C for silica with a 60 Å and 90 Å pore size

originate from different intraparticle porosity and better accessibility inside the pores.

Table 4 The effective intraparticle diffusion coefficients at 30 °C for three different initial concentrations

C_0 [mol/m^3]	1	1.5	2
D_P [m^2/s]	$1.95\cdot10^{-10}$	$1.57\cdot10^{-10}$	$2\cdot10^{-10}$

5.5 Influence of the adsorbate initial concentration

Since it is reported in the literature (Serarols et al. 2001) that concentration can have an influence on the kinetic properties, it is decided to check the influence of the initial $CoCl_2$ concentration. The selected concentration range is 1–2 [mol/m^3]. This very narrow range is of our interest. The experimental data and model results are shown in Fig. 7. The effective pore diffusion coefficients are given in Table 4. As it is observed concentration of the $CoCl_2$ solution in acetonitrile does not have an effect on the value of effective pore diffusion coefficient. Therefore this effect can be disregarded in further modelling of the adsorption process.

5.6 Comparison between polymeric and silica based adsorbents

Diffusion coefficients for the polymeric adsorbents used in the work of Dunnewijk et al. (2006) and for functionalized silica adsorbents studied in this work are given in Table 5. Nomenclature for bi-dispersed Amberlyst A 21 diffusion coefficients is D_a and D_i corresponding to the macro- and micro-pore effective intraparticle diffusivity respectively, while for mono-dispersed particles D_P is kept. Diffusion coefficients for both pore diameters (60 Å and 90 Å) of mesoporous silica are in the same range as diffusion coefficient for macropores, D_a, of the polymeric adsorbent Amberlyst A 21. Diffusion coefficients $8.22\cdot10^{-20}$ and $7.14\cdot10^{-16}$ are of significant different magnitude due to micropores and polymeric matrix found in Amberlyst A 21 and Polymerbound PPh_3. Swelling of Amberlyst A 21 and Polymerbound PPh_3 caused by solvent penetration is also reported by Dunnewijk et al. (2006). These very low diffusion coefficients lead to slow mass transfer and longer residence time in the adsorption column. Therefore it is evident that silica based adsorbents have preferred structure and mass transfer properties compared to polymer ones.

In our previous work (Djekić et al. 2007) it is shown that 2-(2-pyridyl)-functionalized silica has intermediate binding

Table 5 Comparison of intraparticle diffusion coefficients between polymeric [5] and silica based adsorbents

Amberlyst A 21 [5]		Polymerbound PPh_3 [5]	2-(2-pyridyl)ethyl-functionalized silica	
D_a [m^2/s]	D_i [m^2/s]	D_p [m^2/s]	D_p (60 Å) [m^2/s]	D_p (90 Å) [m^2/s]
$1.25 \cdot 10^{-10}$	$8.22 \cdot 10^{-20}$	$7.14 \cdot 10^{-16}$	$1.95 \cdot 10^{-10}$	$5.8 \cdot 10^{-10}$

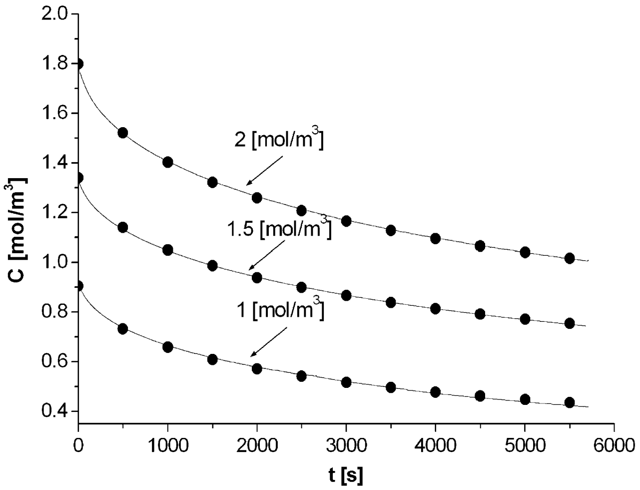

Fig. 7 The experimental (*solid line*) and the model (*full circles*) results of the $CoCl_2$ concentration changes over the time at 30 °C for three different initial concentrations

strength for recovery of $CoCl_2$ which is essential for the RFA application. Amberlyst A21 has a very strong and Polymerbound PPh3 a very weak binding strength (Dunnewijk et al. 2005) for recovery of $CoCl_2$. Therefore they cannot be considered as an optional type of adsorbents for implementation in the RFA.

6 Conclusion

In this paper the effective intraparticle diffusion coefficient of $CoCl_2$ in mesoporous 2-(2-pyridyl)-functionalized silica is determined by using the Zero Length Column method. At sufficiently high flow rates contribution of the external mass transfer resistance is neglected. A mathematical model which is developed to calculate the intraparticle diffusivity for uniform pore distribution silica describes well the adsorption of $CoCl_2$ over time. The values of the diffusion coefficient do not depend on the particle size but only on pore size:

- pore size of 60 Å: $D_p = 1.95 \cdot 10^{-10}$ m^2/s,
- pore size of 90 Å: $D_p = 5.8 \cdot 10^{-10}$ m^2/s.

Particles with 90 Å pore size should be selected for further research because they provide faster diffusion inside particles, and still have equivalent surface area as the one with 60 Å pore size. Since the effective pore diffusion coefficient does not depend on the particle size, but the internal mass transfer rate does, it is recommended to use smaller particle sizes for the adsorption bed. It was also shown that the effective pore diffusion coefficient does not depend on the concentration range (1–2 [mol/m^3]). Due to uniform pore structure and high intraparticle diffusion coefficients silica adsorbents are promising adsorbents for the Reverse Flow Adsorption application.

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