

HYDROGENATION OF NITROTOLUENE USING PALLADIUM SUPPORTED ON CHITOSAN HOLLOW FIBER. INFLUENCE OF EXPERIMENTAL PARAMETERS

Francisco Peirano Blondet, Thierry Vincent, Eric Guibal

Ecole des Mines d'Alès - Laboratoire de Genie de l'Environnement Industriel
6 avenue de Clavieres 30319 Alès cedex FRANCE

Abstract

A continuous catalytic reaction has been tested with chitosan hollow fibers as a support for palladium catalyst for the hydrogenation of aromatic nitro compounds at room temperature and under hydrogen atmospheric pressure. The catalytic fibers were prepared by immobilizing palladium on glutaraldehyde cross-linked chitosan fibers followed by an *in-situ* chemical reduction. Fibers were loaded with increasing amounts of palladium metal. The substrate was pumped through the lumen of the fiber. A low hydrogen pressure was maintained at the outer compartment of the reactor. This allows the necessary diffusion of the reducing agent to the inner surface of the fiber where the Pd catalytic crystals can transfer molecular hydrogen to convert the substrate. Several reaction parameters were tested including: Pd content in the fiber, substrate concentration, flow rate and residence time, temperature and the nature of the solvents. The efficiency of the process was determined by establishing both the conversion yield (%) and TOF (turnover frequency, mmol *o*-toluidine h⁻¹ mg⁻¹ Pd). The conversion percentage determines the efficiency of the process while the TOF normalizes the efficiency of the process as a function of the flow rate and metal content. The palladium content in the fiber must be optimized; increasing the amount of palladium does not proportionally increase the conversion yield and *o*-toluidine production. Palladium excess can produce membrane pore obstruction and can change (a) the size of metal crystals in the fiber and (b) Pd nano particle activity. Changing the solvent, the catalytic efficacy follows the series: methanol > ethanol > isopropanol. This ranking can be correlated to the dielectric coefficient of solvent.

Key words: Chitosan hollow fibers, palladium, catalyst, hydrogenation, nitro toluene

Introduction

Hydrogenation reactions are commonly used for the preparation of intermediary products for fine chemistry. They usually require using supported-catalysts that allow recovering expensive materials at the end of the synthesis route. Though most of the industrial processes use carbon, alumina materials or synthetic polymers for the immobilization of catalytic metals, an increasing number of studies focus on the use of materials of biological origin as support [1]. Many materials of biological origin have been carried out for a wide diversity of reactions including alginate, gelatin, wool, cellulose and chitosan [2]. Chitosan is retaining a growing interest as pointed out by Guibal [3] due to several reasons: (a) high efficiency for metal uptake, (b) chemical versatility; physical versatility. This amino-polysaccharide can bind (a) metal cations by chelation mechanisms on free electronic doublet of nitrogen at near-neutral pH, and (b) metal anions by electrostatic attraction on protonated amine groups in acidic solutions. The possibility to condition chitosan under several forms such as gel beads, fibers, membranes, hollow fibers can be of great interest for designing new processes.

The present study focuses on the screening of experimental parameters (palladium content, solvent, flow velocity, substrate concentration ...) for the catalytic hydrogenation of nitrotoluene (which is converted into *o*-toluidine) using a Pd-catalyst supported on chitosan hollow fibers in alcohol solvent (methanol, ethanol, isopropanol) with hydrogen gas as the hydrogenation reagent.

Material and Methods

Preparation of chitosan hollow fibers

Previously described procedure [4] derived from Agbo and Quin [5] and Modrzejewska and Kaminski [6] has been used for the preparation of chitosan hollow fibers. Chitosan solution with concentration of 7 % was prepared from acetic acid solution (5 % w/w). Afterwards the solution was filtered to remove non-dissolved material and the viscous solution was de-bubbled under vacuum. Then the solution was extruded into an alkaline coagulation bath. The external part of the fiber was neutralized and the inner part of the extruded material was not coagulated. The core of the fiber was removed using first air flow, followed by alkaline treatment. Finally the fiber was rinsed and stored in NaOH solution. The standard length of the fibers used in the study was 0.5 m. The internal diameter of wet fibers was $400 \pm 20 \mu\text{m}$ and the thickness of fiber walls was $80 \pm 5 \mu\text{m}$. This means that for a length of 0.5 m the mean residence time in the fiber was 4.2 s, 6.3 s and 12.6 s for the standard flow rates used in most of the experiments, i.e. 0.9 mL min^{-1} , 0.6 mL min^{-1} and 0.3 mL min^{-1} , respectively. After drying, the internal diameter of the fibers decreased to $200 \pm 15 \mu\text{m}$ and the thickness of fiber walls was $25 \pm 4 \mu\text{m}$. The standard weight of the fiber (for 0.5 m long fibers) was 22.5 mg (dry weight).

Conditioning of chitosan hollow fibers

Because of solubility of chitosan in hydrochloric acid solutions (the solution to be used for palladium immobilization) it is necessary to improve the stability of chitosan fibers using a cross-linking treatment before adsorption process. For the cross-linking of hollow fibers, a diluted solution of glutaraldehyde has been used. Between amine groups of the polymer and the aldehyde functions of the cross-linking agent a Schiff base reaction occurs. When the polymer is conditioned in the form of gel the cross-linking ratio (the ratio between amine groups and aldehyde in the batch mixture) strongly affects its mechanical properties. Indeed, additional bonds between polymer chains make the material more fragile. The cross-linking treatment strongly affects on the breakability of the fibers. The fibers were cross-linked by flowing 50 mL of diluted glutaraldehyde solution (0.25 %) at high velocity (flow rate: 1.5 mL min^{-1} ; flow velocity: $3.5 \cdot 10^3 \text{ m h}^{-1}$) through the lumen of the fibers. It is supposed that high flow velocity facilitates the reaction of the cross-linking agent with the amine groups through the total length of the fiber and prevents the cross-linking not being homogeneous along the fiber.

Palladium sorption and Pd reduction

Palladium chloride solutions were prepared in HCl solutions controlling the pH to 2. This pH was optimum for metal sorption due to favorable electrostatic balance between protonated amine groups of chitosan and anionic chloropalladate species [7]. The palladium solution was flowed through the fiber (under recirculation) at high speed (to facilitate identical yields of Pd sorption through the total length of the fiber). Different amounts of metal have been used (compared to the number of amine groups) to investigate the influence of Pd loading on catalytic efficiency and more specifically to evaluate how this parameter can control the rationale use of Pd (measuring the turnover frequency).

The content of Pd on the fibers was calculated by the mass balance equation (considering the initial and final concentrations of Pd solutions flowing through the fiber) during metal sorption step and compared to mineralized fibers (after Pd reduction, loaded fibers were reacted by concentrated HNO₃ and analyzed for Pd content using ICP-AES analysis). The difference of Pd content using these two methods did not exceed 5 %.

For the palladium reduction treatment hydrogen gas that was produced by reaction of 200 ml of sulfuric acid solution (0.5 N) with 100 mg of zinc as a fine powder has been passed through the fiber for two hours.

Hydrogenation procedure

The hydrogenation module is represented on Figure 1. The solution prepared by dissolving 2-nitrotoluene (Aldrich, Germany) into methanol (ethanol or isopropanol) was pumped through the lumen of the fiber using a peristaltic pump. The fiber was placed in a tube connected to a hydrogen vessel with a pressure gauge. Samples were collected at the outlet of the fiber at fixed times (in most cases the reaction time was 1 hour). The flow rate for hollow fiber feeding was systematically measured and used for the true determination of process efficiency.

Collected samples were analyzed by UV-spectrophotometry to determine UV spectrum. The conversion of nitrotoluene (wavelength of absorbance: 257 nm) into o-toluidine was followed analyzing the concentration of products using a colorimetric analytical method (measurement of the absorbance of the complex at the wavelength: 421 nm). This method consists in the detection of a Schiff's base product obtained by the reaction of a primary aryl amine compound with the Ehrlich reactive (4-dimethylaminobenzaldehyde) [8].

The efficiency of the process was determined by establishing both the conversion yield (%) and the TOF (turnover frequency, mmol o-toluidine h⁻¹ mol⁻¹ Pd). The conversion percentage allows determining the efficiency of the process while the TOF allows normalizing the efficiency of the process in function of flow rate and metal content.

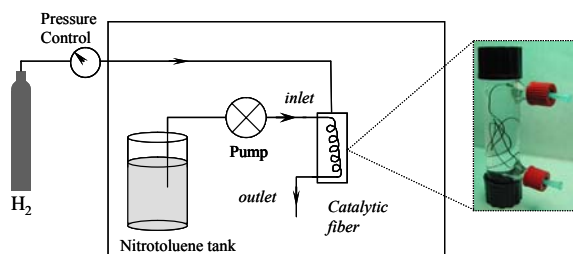


Figure 1 : Experimental setup

Results and Discussion

Experiments were performed to check the influence of the flow rate (F , mL min⁻¹), the substrate concentration (C_0 , mg L⁻¹), the amount of Pd (Pd, mg) per fiber (length: 0.5 m; dry weight: 22.5 mg), hydrogen pressure, solvent and temperature. Their effect was measured through the determination of turnover frequency (TOF: mmol(Pd)mol⁻¹ h⁻¹) and conversion yield (concentration of o-toluidine produced compared to initial concentration of nitrotoluene).

Influence of flow rate (F):

The flow rate of the substrate solution controls its mean residence time (i.e. 12.6 s, 6.3 s and 4.2 s for flow rates of 0.3, 0.6 and 0.9 mL min⁻¹, respectively). Changing the residence time obviously influenced the catalytic performance as shown in Figure 2. The TOF increased as the flow rate increased, regardless of the initial concentration of the substrate. However, this increase is mostly significant for low Pd content, while the difference observed for the different series tended to decrease with increasing Pd amount on the fiber (specifically for Pd amount greater than 1.5 mg/fiber). Increasing the residence time allows a greater time for the catalytic system to convert nitrotoluene into o-toluidine. Increasing the content of palladium reduced the impact of residence time: the presence of large excess of Pd crystals diminishes the impact of kinetic limitations due to hydrogenation kinetics, or may improve diffusion of hydrogen by jumping between close Pd crystals. The TOF is a measurement of the efficacy of the use of catalytic metal. As expected increasing Pd content involved a decrease in TOF.

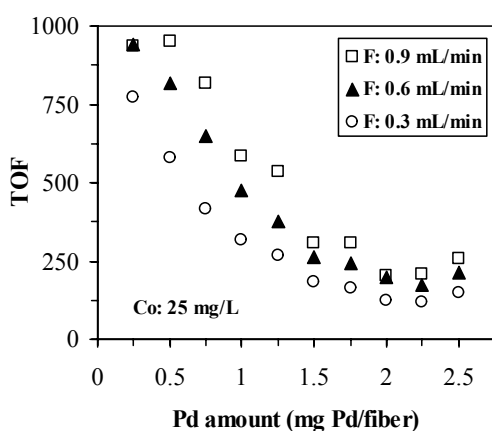


Figure 2 : Influence of flow rate on TOF (mmol (Pd)mol⁻¹ h⁻¹) for nitrotoluene hydrogenation (P(H₂): 1 bar; room temperature; solvent: methanol) at different initial concentrations of substrate (Co: mg L⁻¹) and for fibers loaded with different Pd amounts (Pd: mg per fiber).

Influence of substrate concentration (Co):

Figure 3 shows the impact of initial concentration of nitrotoluene (Co, mg L⁻¹) on the TOF for fibers loaded with different amounts of Pd. As expected the TOF increases with increasing the initial concentration of the substrate; however, the influence of substrate concentration decreased with increasing the amount of Pd on the catalytic fiber. At low Pd content (i.e. 0.5 mg Pd/fiber) the TOF increased by 3 to 4 times when increasing nitrotoluene concentration from 25 to 100 mg L⁻¹; while at high Pd content (i.e. greater than 1.5 mg Pd/fiber) the variation did not exceed 10 %. Increasing Pd content tended to level the TOF variation.

The influence of nitrotoluene concentration on the production of o-toluidine is shown on Figure 4. The production of o-toluidine was little affected by Pd content (above 0.5 mg Pd/fiber) but linearly increased with nitrotoluene concentration with a slope that increased with flow rate.

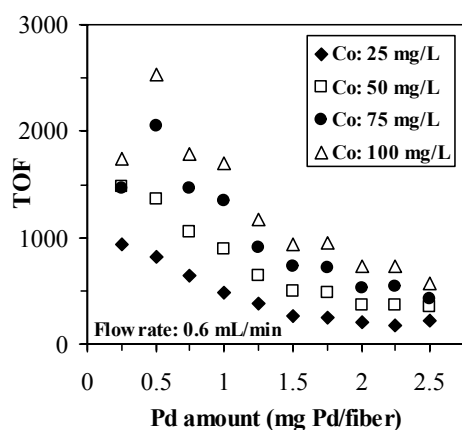


Figure 3 : Influence of initial substrate concentration on TOF ($\text{mmol (Pd)mol}^{-1} \text{h}^{-1}$) for nitrotoluene hydrogenation ($\text{P(H}_2\text{)}$: 1 bar; room temperature; solvent: methanol) at different flow rate (F : mL min^{-1}) and for fibers loaded with different Pd amounts (Pd: mg per fiber).

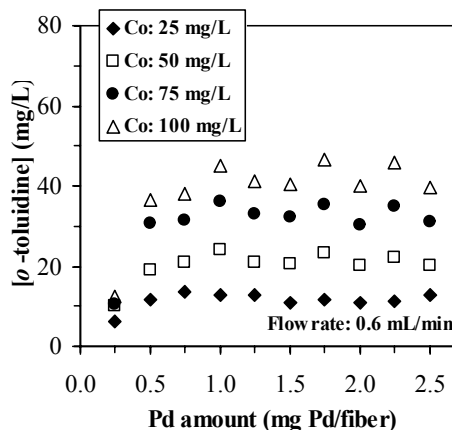


Figure 4 : Influence of initial substrate concentration on *o*-toluidine production (concentration mg L^{-1}) for nitrotoluene hydrogenation ($\text{P(H}_2\text{)}$: 1 bar; room temperature; solvent: methanol) at different flow rate (F : mL min^{-1}) and for fibers loaded with different Pd amounts (Pd: mg per fiber).

Influence of Pd content in the fiber (Pd):

Previous sections have shown that the content of Pd on the fiber was not a critical parameter for the determination of conversion yield and for *o*-toluidine production, at the notorious exception of low Pd content (0.25 mg Pd/fiber). Basically, the efficiency of the process is weakly controlled by the amount of Pd immobilized on the catalytic support; however, this may influence the accessibility and the effective reactivity of Pd crystals. The major impact of these parameters can be observed on the TOF ($\text{mmol (Pd) mmol}^{-1} \text{h}^{-1}$) that measures the effectiveness of metal use. Figure 5 shows that the TOF increased linearly with nitrotoluene concentration (except for fibers with the lowest Pd content, i.e. 0.25 mg Pd/fiber), whatever the flow rate, while it decreased with increasing the amount of Pd immobilized on the fibers.

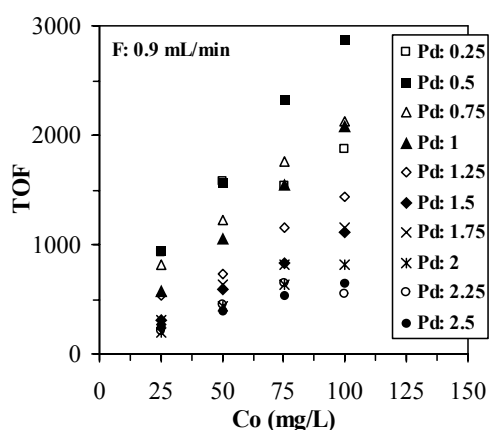


Figure 5 : Influence of Pd content on TOF ($\text{mmol (Pd)mol}^{-1} \text{h}^{-1}$) for nitrotoluene hydrogenation ($\text{P(H}_2\text{)}$: 1 bar; room temperature; solvent: methanol) at different flow rates (F , mL/min) and different initial substrate concentrations (Co , mg/L).

This result clearly demonstrates that it is not necessary to immobilize huge amounts of metal on the fiber: the presence of an excess of Pd crystals did not increase conversion yield nor *o*-toluidine production but reduces the global effectiveness of metal use. The highest values for TOF were obtained with a Pd content of 0.5 mg Pd/fiber; this means a Pd content of about 2.25 %. The TOF increased for this optimum Pd content with increasing both nitrotoluene concentration and flow rate: the highest TOF tended to $3000 \text{ mmol (Pd)mmol}^{-1} \text{h}^{-1}$ for F : 0.9 mL min^{-1} and Co : 100 mg L^{-1} .

Influence of solvent (S)

The solvent strongly influences the solubility of hydrogen. To check the influence of this parameter, a series of experiments was performed with methanol, ethanol and isopropanol, at room temperature under a 1-bar hydrogen pressure with variable amounts of Pd (0.5, 1, 1.5 and 2 mg Pd/fiber) and variable flow rate (0.3, 0.6 and 0.9 mL min⁻¹), as shown on Figure 6. The TOF was obviously controlled by the type of solvent used for the experiments. The influence of flow rate was also strictly dependent on the solvent: with isopropanol increasing the flow rate of substrate hardly affected the TOF while for methanol and ethanol the TOF increased with flow rate. Regardless of the flow rate the solvents can be ranked in the following order:

Methanol >> Ethanol >> Isopropanol

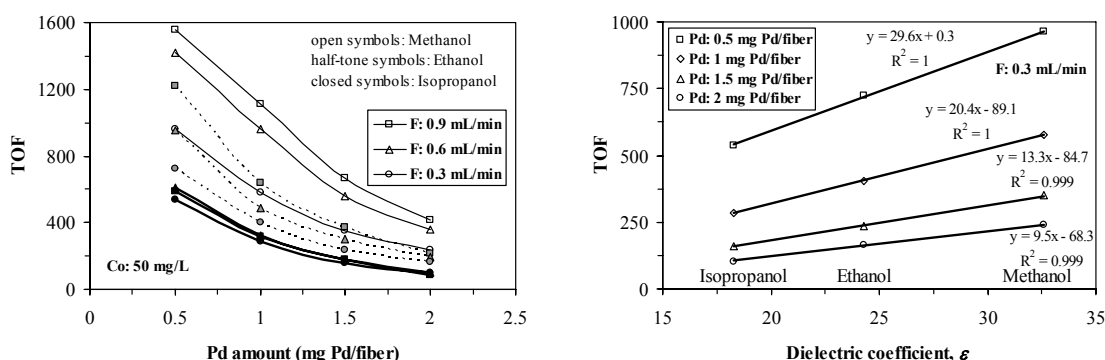


Figure 6 : Influence of solvent on TOF (mmol (Pd)mol⁻¹ h⁻¹) for nitrotoluene hydrogenation (P(H₂): 1 bar; room temperature) at different flow rates (F, mL/min) and Pd contents (mg Pd/fiber) and correlation between TOF and solvent dielectric coefficients.

The values of TOF were correlated to the dielectric coefficients (ϵ , or relative permittivity [9]); Figure 6 shows for a flow rate of 0.3 mL min⁻¹ that, regardless of Pd content, the TOF linearly increased with the dielectric coefficient of the solvent. Similar correlations were obtained with other flow rates (not shown). Solvent effects on hydrogenation reaction have been extensively studied [10]: most of studies showed that the dielectric coefficient influences the enantioselectivity of the reaction (e.e.): increasing ϵ decreased e.e.; the literature is more controversial on the influence of dielectric coefficient on the hydrogenation rate.

Influence of temperature (T)

The temperature is also a key parameter for hydrogen solubility [11], and for solvent dielectric coefficient. Increasing the temperature of the reaction increases the solubility of hydrogen in methanol while it decreases the dielectric coefficient. The temperature can then induce contradictory effects on the reaction: enhancement due to increased hydrogen solubility, decrease due to diminished dielectric coefficient. Figure 7 shows the impact of temperature on TOF for selected experimental conditions. Increasing the temperature increased the TOF. The increasing trend was steeper at low temperature (in the range 10-40 °C) and tended to stabilize at higher temperature (above 40 °C, up to 60 °C).

Based on the Arrhenius equation the TOF was also plotted in function of the reciprocal of absolute temperature. The distribution of experimental data shows that the TOF followed the expected exponential trend of the Arrhenius equation in the range 10-40 °C (283-313 K), while above 40 °C, the plot showed a change in the slope of the curve that tended to level off. For values greater than

50 °C, the temperature is getting closer to boiling temperature of methanol, which in turn can cause changes in transfer properties (viscosity, diffusion ...) of the solvent. In the range of temperature 10-40 °C, the TOF can be described by the equation:

$$\text{TOF} = A e^{-\frac{k}{T}} = A e^{-\frac{\Delta H}{RT}} = 55415 e^{-\frac{1,474.6}{T}} = 55415 e^{-\frac{12,254}{RT}}$$

where ΔH is the activation energy (kJ mol^{-1}), T the absolute temperature (K), R the ideal gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$). Based on these results, the activation energy was found close to 12.3 kJ mol^{-1} .

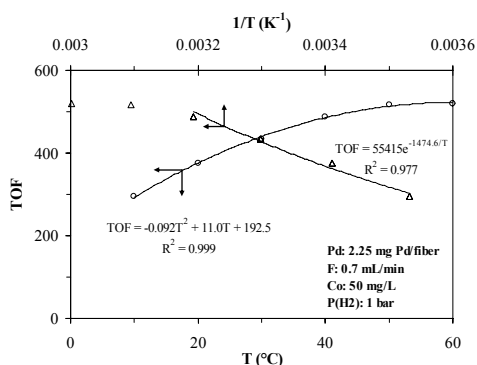


Figure 7 : Influence of reaction temperature on TOF for nitrotoluene hydrogenation under selected experimental conditions.

The increase in catalytic activity with increasing the temperature may be correlated to (a) the enhanced solubility of hydrogen in methanol, (b) the decreased viscosity of methanol (containing the substrate and the products of the reaction), which may influence diffusion of the substrate inside the hollow fiber and thus accessibility to catalytic Pd crystals. This result is partly conflicting with intermediary conclusions regarding the influence of the solvent and hydrogen pressure. The weak effect of hydrogen pressure was interpreted by the weak effect of hydrogen solubility; the significant effect of temperature may be indicative that this parameter is not negligible and that the weak impact of hydrogen pressure can be explained by a weak variation of hydrogen pressure that masked the potential effect of this parameter. On the other hand, changing the solvent has shown that the catalytic performance linearly increased with the dielectric coefficient, increasing the temperature is expected to decrease the dielectric constant of methanol; the results of this section indicate that the catalytic efficiency did not decrease, despite the decrease of dielectric coefficient. The key parameter seems to be the solubility of hydrogen in methanol, rather than its dielectric coefficient.

Conclusion

Hollow fibers made of chitosan can be used for the immobilization of Pd prior to its in-situ reduction. The catalytic hollow fibers are efficient for the hydrogenation of nitrotoluene into o-toluidine under mild conditions: low hydrogen pressure and low temperature. The substrate is pumped through the lumen of the fiber while a low hydrogen pressure (1 bar) maintained at the outer compartment of the reactor allows on-demand diffusion of the reducing agent at the inner surface of the fiber where Pd catalytic crystals can transfer molecular hydrogen to convert the substrate. Increasing the amount of Pd slightly increased conversion yield and o-toluidine production but significantly decreased the turn-over frequency of the system (TOF). An intermediary Pd content (Pd, around 1-1.5 mg Pd/fiber, i.e. around 4-5 % of Pd in dry weight) is

sufficient to maintain optimum activity and avoid poisoning of the catalytic system at long operating time (1 week) (not shown). The temperature controls hydrogen solubility: increasing the temperature enhances the catalytic reaction. Additionally, comparing the influence of solvents the catalytic efficiency obeys the following ranking: methanol > ethanol > isopropanol; actually the TOF can be correlated to the dielectric coefficient of the solvent.

Acknowledgements

Authors thank ANVaR (Agence Nationale de Valorisation de la Recherche) for funding the project CHITO-CAT.

References

- [1] M. Kralik and A. Biffis, Catalysis by metal nanoparticles supported on functional organic polymers, *J. Mol. Catal. A: Chem.*, 177 (2001) 113.
- [2] A.V. Kuchеров, N.V. Kramareva, E. Finashina, A.E. Koklin and L.M. Kustov, Heterogenized redox catalysts on the basis of the chitosan matrix. 1. Copper complexes, *J. Mol. Catal. A: Chem.*, 198 (2003) 377.
- [3] E. Guibal, Heterogeneous catalysis on chitosan-based materials: A review, *Prog. Polym. Sci.*, 30 (2005) 71.
- [4] E. Guibal, T. Vincent and R. Navarro Mendoza, Synthesis and characterization of a thiourea-derivative of chitosan for platinum recovery, *J. Appl. Polym. Sci.*, 75 (2000) 119.
- [5] Q.C. Agboh and Y. Qin, Chitin and chitosan fibers, *Polym. Adv. Technol.*, 8 (1997) 355.
- [6] Z. Modrzejewska and W. Kaminski, Separation of Cr(VI) on chitosan membranes, *Ind. Eng. Chem. Res.*, 38 (1999) 4946.
- [7] M. Ruiz, A. Sastre and E. Guibal, Palladium recovery from dilute effluents using glutaraldehyde cross-linked chitosan, *React. Funct. Polym.*, 45 (2000) 155.
- [8] J.E. Barney, S.R. Harvey and T.S. Hermann, Systematic studies of chromogenic reagents for detecting organic compounds on thin-layer chromatograms: I. Primary, secondary, and tertiary amines, *J. Chromatogr. A.*, 45 (1969) 82.
- [9] E. Toukoniitty, P. Mäki-Arvela, J. Kuusisto, V. Nieminen, J. Päivärinta, M. Hotokka, T. Salmi and D.Y. Murzin, Solvent effects in enantioselective hydrogenation of 1-phenyl-1,2-propanedione, *J. Mol. Catal. A: Chem.*, 192 (2003) 131.
- [10] R. Bisignani, S. Franceschini, O. Piccolo and A. Vaccari, The solvent effect in the enantioselective hydrogenation of (*E*)-2-methyl-2-butenic acid with cinchonidine doped Pd/Al₂O₃, *J. Mol. Catal. A: Chem.*, 232 (2005) 161.
- [11] C. Descamps, C. Coquelet, C. Bouallou and D. Richon, Solubility of hydrogen in methanol at temperatures from 248.41 to 308.20 K, *Thermochim. Acta*, 430 (2005) 1.