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# Chitosan-Supported Palladium Catalyst. 5. Nitrophenol Degradation Using Palladium Supported on Hollow Chitosan Fibers

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Hollow chitosan fibers were reacted with chloro-palladate solutions and subsequently reduced by hydrogen produced in situ by reaction of sulfuric acid with zinc powder in order to manufacture palladium supported on catalytic hollow chitosan fibers ( $C^2HF-Pd$ ). This catalytic support was used to degrade 3-nitrophenol (3-NP) using two different hydrogen donors (hydrogen gas and sodium formate). The solution was flowed through the lumen of the fiber, while the sodium formate was recirculated round the outside of the fiber. In the case of hydrogen gas, the gas was maintained under controlled pressure outside the fiber. The influence of the pH, residence time (ca. flow velocity), nitrophenol concentration, and hydrogen-donor concentration (or pressure) was investigated for both systems in order to evaluate the limiting parameters. While the system using sodium formate was the most efficient for nitrophenol conversion, the system using hydrogen gas avoided the production of secondary waste solutions (formate solutions with traces of nitrophenol, which pass through the fiber membrane).

## Introduction

Phenolic compounds are frequently found in industrial wastewaters, especially as subproducts of the synthesis of pesticides, herbicides, insecticides, dyes, in paper processing, and in the pharmaceutical and petrochemical industries. The United States Environmental Protection Agency (U.S. EPA) lists nitrophenols among the top 114 organic pollutants. Adsorption remains the technique most frequently used for the treatment of nitrophenol-containing solutions using, for example, conventional sorbents such as activated carbon (1) or alternative materials such as clinoptilolite (2) or charred sawdust (3). However, these techniques usually generate toxic slurries that remain technically or economically difficult to eliminate. For these reasons, alternative processes have recently been developed aiming to degrade phenolic compounds into more environmentally friendly products instead of causing a simple pollution transfer (as occurs with sorption processes). Chemical and photochemical oxidation processes have been recently developed (4–8). Catalytic processes using palladium-supported materials have also been studied for the degradation of nitrophenol (9–12).

Supported catalysis is usually carried out on alumina, silica, or activated carbon supports (13, 14). However, many recent studies have focused on the use of polymers for supporting catalytic metals (15–17). Indeed, the versatility

of polymeric materials (conditioning, modification) may be of great benefit for the design of catalytic systems. Because of their stereospecificity, these polymeric materials can add selectivity to the reactions (18).

Biopolymers have received a great deal of attention since they can be used for the separation of optical isomers (19–21). Chitosan, which is produced by alkaline deacetylation from chitin (the most abundant polymer in nature after cellulose), is a typical example of such a versatile and highly functional polymer used for the chiral separation of isomers (22, 23). This polymer is characterized by its high affinity for metal ions. Indeed, the presence of amine groups causes strong interactions with metal cations through chelation mechanisms (24–27) and also interesting ion exchange properties for the uptake of metal anions (26, 28, 29). Chitosan has a very high affinity for precious metals and sorption capacities as high as 3 mmol of metal  $g^{-1}$  are obtained with platinum and palladium (30, 31). Being soluble in most inorganic and organic acids, the biopolymer is usually cross-linked prior to contact with acidic solutions (32).

During the past decade, chitosan has been investigated for catalytic applications in several fields such as the synthesis of fine chemicals (33–38) and also for environmental applications (39, 40). Supported palladium catalysts are very efficient for the dehalogenation and dearomatization of chlorophenols (9, 41, 42). Recently, chitosan-supported palladium catalyst was tested for chromate reduction (39), the degradation of chlorophenol (40), and also the degradation of nitrophenol (43) using sodium formate as the hydrogen donor. The catalysts were prepared by a two-step procedure consisting in the sorption of precious metals on the sorbent, appropriately conditioned (to avoid polymer dissolving in acidic solutions), and followed by a chemical reduction of palladium. Chlorophenol is degraded into phenol and cyclohexanol and/or cyclohexanone (44–46). Nitrophenol is reduced by hydrogenation to aminophenol. After long contact time, complementary products may be obtained in default of a reducing agent. These preliminary studies led to the conclusion that the catalytic reaction is limited to the external surface of the catalyst, mainly due to diffusion limitations (related to the low porosity of the material). For this reason, a new conditioning process for the biopolymer was designed in the form of thin hollow fibers made of chitosan. Indeed, another interesting property of chitosan is its physical versatility. The material can be conditioned in a wide variety of physical forms such as gel beads (47), sponges, membranes, fibers (48), and hollow fibers (49). The catalytic metal was sorbed on the fiber and then reduced, and the resulting catalytic hollow fiber was used for the degradation of nitrophenol. The solution was pumped through the lumen of the fiber, while the hydrogen donor was maintained outside the fiber. In the case of sodium formate, the reactive solution was recycled with appropriate pH control of the solution, while in the case of hydrogen used directly as a gas, the pressure was maintained constant throughout the process.

The present work focuses on investigation of the effect of process parameters on the efficiency of 3-nitrophenol (herein called NP) degradation using a palladium catalyst supported on hollow chitosan fibers ( $C^2HF-Pd$ ). Among the main parameters considered for the optimization of the process we can list the pH, concentration of sodium formate (or the pressure of hydrogen), and concentration of nitrophenol. The efficiency of the process was determined at different flow rates, varying the mean residence time of the solution inside the fiber.

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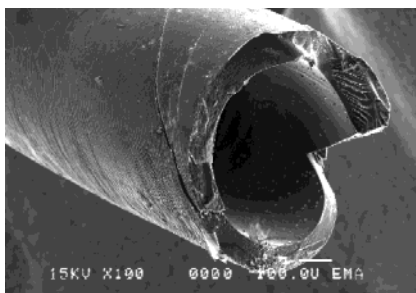


FIGURE 1. Scanning electron microscopy (magnification: 1750 $\times$ ) of chitosan hollow fiber.

## Material and Methods

**Materials.** Chitosan was supplied by Aber Technologies (Plouvien, France). It had previously been characterized (47): the degree of deacetylation was 87%, and the molecular weight was 125 000 g mol<sup>-1</sup> (molecular weight of equivalent monomer unit, 166 g mol<sup>-1</sup>).

NaBH<sub>4</sub> and nitrophenol (3-NP) were purchased from Fluka (Switzerland) as analytical-grade products. PdCl<sub>2</sub> was purchased from Acros (U.S.A.). Other reagents (acids, zinc, HCOONa) were supplied by Carlo Erba (Italy).

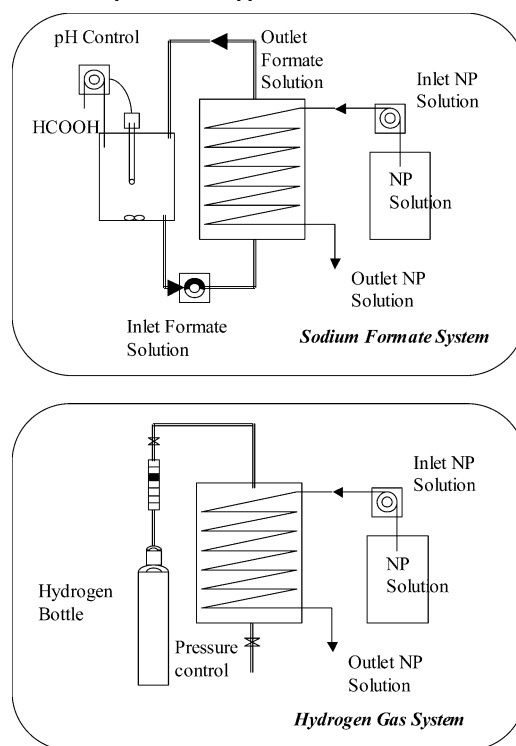
**Hollow Fiber Preparation.** The preparation of chitosan hollow fibers has been described in a previous paper (49). The main steps in the manufacturing process are described below. Hollow fibers of chitosan were produced by casting a viscous chitosan solution (in acetic acid) into a coagulating bath using a procedure derived by Kaminski et al (50), and Agboh and Qin (48). To produce the solution, the chitosan was ground and the smallest particle size (diameter below 125  $\mu$ m) was dissolved in an acetic acid solution, keeping a small excess of organic acid compared to the molar concentration of amine groups. Typically the solution was 4% w/w in both chitosan and acetic acid. The solution was then filtered to remove undissolved or colloidal particles. The solution was de-bubbled, and then the polymeric solution was dropped in a tank maintained at constant air pressure (4 bar). The solution was then extruded into a coagulating bath. After external coagulation, the lumen of the fiber was emptied by withdrawing non-coagulated chitosan by means of airflow followed by water flow. The final fiber was obtained by treatment with alkali. Finally, fibers were dried at room temperature. The external diameter of the fiber was 1.1  $\pm$  0.1 mm, and the thickness of the fiber wall was 0.1  $\pm$  0.015 mm. Figure 1 shows scanning electron micrographs of the fibers after air drying.

**Palladium Sorption.** As chitosan is soluble in acetic solutions and the sorption of precious metal is only effective in acid solutions (30, 31), it was necessary to precondition the fibers. Usually, glutaraldehyde is used for the reinforcement of chemical stability of chitosan in acid solutions (32). However, this reaction has a serious drawback in the case of hollow fiber preparation; it makes the fiber very brittle, and it was preferable to condition the fiber in a sodium sulfate solution (1 g L<sup>-1</sup>) at natural pH. The fiber was then put in contact with a palladium chloride solution (200 mg Pd L<sup>-1</sup>) at pH 2 overnight. Finally, the fiber was rinsed with water.

**Procedure for Palladium Reduction.** The reduction treatment consisted in bringing the loaded sorbent (200 mg) into contact with 100 mL of a sulfuric acid solution (1% w/w) mixed with 300 mg of zinc (provided as a fine powder). The fiber was maintained in the reducing bath until hydrogen bubbling stopped. The fiber was finally dried at room temperature.

A sample of the fiber was digested with a mixture of sulfuric acid (1 mL, 36 M) and hydrogen peroxide (0.5 mL, 10 M) in order to completely degrade the support and dissolve

## SCHEME 1. Experimental Apparatus



palladium for the analysis of metal content using an inductively coupled plasma atomic emission spectrometer (ICP-AES JY2000, Jobin Yvon, Longjumeau, France). The palladium content in the fiber was determined as 4.2% (w/w); this value was consistent with that obtained using the mass balance equation for the sorption procedure: the decrease of the concentration of palladium in the solution was used to determine the amount of sorbed metal. The water content of the fiber (after rehydration) was 62%. The length of the fibers (hydrated) used for these experiments was set at 1.3 m; the internal diameter was 500  $\pm$  15  $\mu$ m. The internal volume of the fibers was 273  $\pm$  5  $\mu$ L. The amount of palladium present on the fiber was 4.09 mg (for a total fiber mass of approximately 97.5 mg).

Analysis by X-ray photoelectron spectroscopy (XPS) showed that the reduction procedure using hydrogen produced by reaction of sulfuric acid on zinc powder only enabled partial reduction of the metal catalyst powder (Vincent and Guibal, 2002). Palladium was present in two forms (identified by XPS peaks at 336.2 eV and 337.8 eV) corresponding to the forms Pd(II) and Pd(0), respectively.

Transmission electron microscopy (TEM) was used to measure the size of catalyst particles at the surface (and in the mass) of the polymer (in the form of flakes). The distribution of palladium granules was almost homogeneous, though a gradient was detected between the external part of the particles and the center of the catalyst. The size of metal granules was measured at close to 4–5 nm. The size of metal particles is a key parameter in the catalytic activity of the material (42).

**Procedure for Nitrophenol Degradation.** The ends of the catalytic fiber were connected to thin nozzles fed with a solution pumped from the nitrophenol solution reservoir, and the fibers were arranged in a closed tube connected to a tank of sodium formate or a bottle of hydrogen gas (see Scheme 1).

In the case where sodium formate was used as the hydrogen donor, the formate solution was recycled and its pH controlled at pH 4 using formic acid. Samples were collected at the outlet of the fiber, and the nitrophenol

concentration was determined every 15 min by a spectrophotometric method using a Varian 2050 spectrophotometer. To prevent changes in the shape of the UV spectra of the products of the reaction with changes in the pH (in the course of the reduction process) a drop of 100  $\mu$ L of 1 M sulfuric acid was systematically added to collected samples before analysis. The absorbance of the solution was measured at 331 nm and compared to standard solutions. A typical experiment lasted for 1 h, i.e., four samples were collected in order to check the evolution of the efficiency of the process. The concentration of nitrophenol in the sodium formate solution was also measured at the end of the experiment to check the transfer of the phenolic compound through the fiber. Mass balance on nitrophenol was used to evaluate the mean conversion yield, taking into account the concentration of phenolic compound in both formate solution and treated effluent and the volume of solution actually treated. The degradation efficiency was obtained by a mass balance equation (as the ratio of nitrophenol degraded to the initial concentration of the phenolic compound), and the catalytic activity (mmol NP h<sup>-1</sup> g<sup>-1</sup> Pd) was obtained taking into account the degradation efficiency (DE), the initial concentration (C<sub>0</sub>, mg L<sup>-1</sup> or mmol L<sup>-1</sup>), the volume of solution passed through the fiber (V, L), and the amount of palladium present on the fiber (i.e.,  $m_{Pd}$ , 4.09 mg)

$$CA = \frac{DE \times C_0 \times V}{m_{Pd}}$$

In the case where hydrogen gas was used as the hydrogen donor, the same experimental procedure was used but in this case the residual concentration of nitrophenol was only measured at the outlet of the fiber. Nitrophenol degradation efficiency was obtained by comparing the outlet and inlet concentrations, and the catalytic activity was obtained using a similar mass balance as was used for the calculations in the sodium formate system. For each experimental series the catalytic activity was determined, and the parameters are given in Tables 1–4 in the Supporting Information.

Test experiments were performed to check the actual influence of catalyst and hydrogen donor. Fibers without palladium and catalytic fibers without hydrogen donor were tested to verify that sorption on the raw fiber (and on the metal-impregnated fiber) was negligible compared to the conversion efficiency of the catalytic fiber under standard operating conditions.

## Results and Discussion

**Products of the Reaction.** In the case of nitrophenol degradation on catalyst flakes in a batch system it appeared that the process can be separated into (at least) two steps: (a) the reductive hydrogenation of nitrophenol into aminophenol, (b) the oxidation of aminophenol into subproducts that depend on experimental conditions (for example, muconic acid and oxidized derivatives) (43). The transformation of 3-NP led to the same degradation products as 3-AP, while 2-NP and 4-NP gave the same degradation products as 2-AP. Therefore, the position of the substituents on the phenolic ring strongly controls the products of the reaction. The second step usually occurred after 45–60 min contact time (after consumption of the sodium formate and the disappearance of reductive conditions); the complete degradation of AP usually required several hours of contact under the selected experimental conditions (at least 24 h). Since, under similar experimental conditions, phenol is not substantially degraded, it seems that the degradation of aminophenol does not occur through production of phenol (as an intermediate product) followed by its subsequent degradation. The degradation of aminophenol may only occur during the substitution steps on amino groups;

therefore, the orientation of the reaction is controlled by the position of the substituents on the phenolic ring. The homogeneous hydrogenation of aromatic nitro compounds by palladium–synthetic polymer complexes was investigated using hydrogen gas, and several compounds were identified as reaction products, including aminophenol and hydroxyaniline (51, 52). On a Pd/carbon catalyst, in the presence of hydrogen gas, Choudhary et al. (10) only observed aminophenol formation during the hydrogenation of nitrophenol. The same hydrogenation product was obtained using a Pt/C catalyst by reaction of hydrogen gas on nitrophenol solution (12). In the case of nitrotoluene hydrogenation using palladium supported on alumina material and hydrogen gas as the hydrogen donor, several complex mechanisms have been identified with intermediary products (53).

In the case of C<sup>2</sup>HF–Pd system, the ratio Pd/nitrophenol and contact time are significantly different and more favorable to a strong conversion of nitrophenol into aminophenol. The short contact time and the experimental procedure are more favorable for maintaining reductive conditions. Therefore, the oxidation of aminophenol, which was observed under certain conditions in batch systems, did not occur with the hollow fiber system. The analysis of the solutions at the outlet of the hollow fiber only showed the typical UV profile of aminophenol. The hollow fiber system appears to be more “selective”.

**Influence of pH.** The pH is an important variable in the evaluation of catalytic reactions since it affects surface charge, dissociation of the substrate, and also dissociation of the hydrogen donor when it is a chemical reagent (hydrogen transfer mechanism). Indeed, depending on the surface properties of the catalyst, its overall charge may control the sorption of the substrate or that of the hydrogen donor. It may also influence the desorption kinetics of the products of the catalytic reaction. Chitosan is characterized by its intrinsic pK<sub>a</sub>, which depends on its degree of deacetylation. For the chitosan sample used in this study, the pK<sub>a</sub> was close to 6.4. Below pH 5–5.5, more than 90% of amine groups are protonated and thus available for sorption of anionic species. Since the pK<sub>a</sub> of the formic acid/formate couple is close to 3.8, formate anions are adsorbed in the pH range 3–5.5. The pK<sub>a</sub> of nitrophenol is close to 7.1. Nitrophenolate is only predominant in neutral or alkaline solutions, but under these pH conditions, chitosan is almost completely deprotonated. Previous experiments on catalytic powders have shown that nitrophenol degradation is optimum at low pH, between 3 and 4 (43). Since the fibers cannot be cross-linked using glutaraldehyde (since this process leads to brittle fibers), the fibers were preconditioned using sulfate. In this case the chemical stability of the fibers was lower. For this reason, the initial pH was only varied between 4 and 6.

For both sodium formate and hydrogen gas systems, the pH increased during the degradation of nitrophenol. The pH variation depended on experimental conditions. However, in most cases the pH varied by less than 1.5 units. This is significantly lower than the pH variations that were observed in the case of chlorophenol and nitrophenol degradation (40, 43). Gallezot et al. have shown that formic acid can be totally oxidized (into CO<sub>2</sub>) by a Pt/C catalyst and that this reaction is accompanied by a strong increase in the pH, shifted under selected experimental conditions (atmospheric air pressure, 50 °C), from pH 3 to 5.5 (54). The pH of sodium formate solution also varied during the degradation process, and preliminary experiments performed without pH control showed a significant decrease in the efficiency of the catalytic systems. The system was then modified by the addition of a pH control loop in the recirculating flow of sodium formate (at the selected pH value, i.e., pH 4).

Figure 2 shows that increasing the pH of the solution decreased the efficiency of nitrophenol degradation when

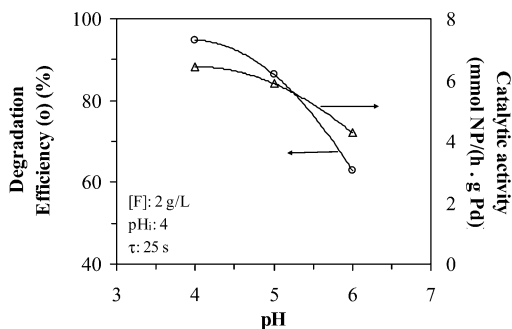


FIGURE 2. Influence of pH on 3-NP degradation efficiency and catalytic activity.

sodium formate was used as the hydrogen donor. The decrease was especially significant above pH 5. This is consistent with results obtained in batch systems with catalyst powder (43). Increasing the pH decreases sorbent protonation, which in turn decreases the reactivity of the material for sorption of formate and/or nitrophenol. Nitrophenol transfer from the aqueous solution to the sodium formate solution compartment varied with the pH but never exceeded 3 mg NP L<sup>-1</sup>, which means that less than 3% of the total amount of nitrophenol passed through the fiber. It is also important to observe that throughout the procedure the efficiency of the process remained stable for the experiments performed with initial pH 4 but significantly decreased at other pHs, from 93% to 90% at pH 5 and from 80% to 60% at pH 6. The efficiency significantly decreased at near-neutral pH, possibly due to poisoning of the catalyst (accumulation of intermediary or final products at the surface of the catalyst) or an increased pH variation that brought the solution to a pH value (up to pH 6.4) for which the catalyst was not active. The catalytic activity also slightly decreased with increasing the pH (Figure 2).

The exact mechanism of formate action has not been completely elucidated, and two possible mechanisms are frequently cited for the interpretation of chlorophenol and nitrophenol conversion: (a) reaction of hydrogen produced during formate decomposition or (b) hydrogen transfer. The influence of the pH on nitrophenol degradation using hydrogen gas was not investigated, but for further experiments the initial pH was selected at pH 4 for both systems.

This preliminary study enabled verification of the suitability of a chitosan-supported palladium catalyst for use as a catalytic material for the environmentally friendly degradation of nitrophenol using this specially tailored conditioning of the support (hollow fiber). These results confirm previous conclusions reached using chitosan flakes. However, this new conditioning process increased catalytic activity compared with the flaked material, up to 5 times greater under some of the selected experimental conditions. Moreover, the use of this conditioning process enabled better control of experimental conditions (pH, control of sodium formate and substrate concentrations) and reduced the effect of some parameters, such as the size of catalyst particles, which was shown to be a limiting parameter in the case of flaked materials (the reaction occurring only at the periphery of the particle). It also allowed hydrogen gas to be used as the hydrogen donor.

**Influence of Nitrophenol Concentration.** The concentration of nitrophenol was varied and the mean degradation efficiency measured at a given mean residence time for both the sodium formate (Figure 3) and the hydrogen gas system (Figure 4). The systems were considered at short and long residence times in order to evaluate the contribution of reaction kinetics (limitations due to insufficient contact time) on the influence of nitrophenol charge on conversion percentage. Under the selected experimental conditions (i.e.,

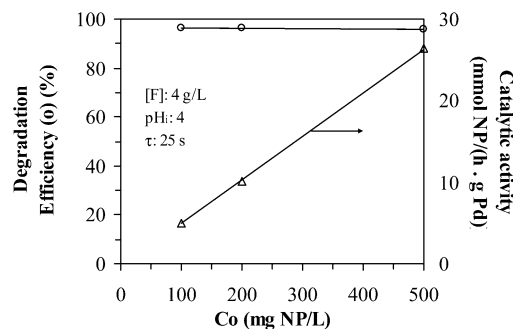


FIGURE 3. Influence of nitrophenol concentration (Co) on degradation efficiency and catalytic activity using sodium formate as the hydrogen donor.

sodium formate in large excess at a concentration of 4 g L<sup>-1</sup>, the mean degradation efficiency was not controlled by the concentration of phenolic compound, at least in the selected concentration range (i.e., 100–500 mg NP L<sup>-1</sup>) for long contact time (i.e.,  $\tau \approx 25$  s). The mean conversion rate exceeded 95% regardless of the initial concentration. The degradation efficiency was measured every 15 min (for 1 h), and in the case of the 500 mg NP L<sup>-1</sup> solution the degradation efficiency progressively decreased from 85% to 78%, while it remained constant for the other initial concentrations. This is indicative of limitations due to either (a) a lack of hydrogen donor or (b) a limitation of reaction kinetics (residence time was not high enough to allow the complete conversion of the substrate). The concentration of nitrophenol transferred through the membrane during the operation increased with increasing nitrophenol concentration but remained relatively low at below 2 mg NP L<sup>-1</sup> (corresponding to a nitrophenol transfer lower than 1% of total nitrophenol passed through the fiber). When the contact time was shortened (i.e.,  $\tau \approx 12$  s), the substrate concentration had a more marked effect. The catalytic activity was strongly influenced by the initial concentration of nitrophenol: it varied linearly with Co. Increasing the concentration of the substrate enhanced its sorption, which in turn improved its degradation. The catalyst (the catalytic metal) was more efficient with high initial nitrophenol concentration. Catalytic activity exceeded 26 mmol NP h<sup>-1</sup> g<sup>-1</sup> Pd at the highest substrate concentration (i.e., 500 mg NP L<sup>-1</sup>).

In the case where hydrogen gas was used as the hydrogen donor, the diffusion of hydrogen through the catalytic membrane seemed to be high enough to give sufficient hydrogen to hydrogenate the substrate. In this case, there was no transfer of nitrophenol to the outlet side of the membrane. The pH of the substrate also increased, but the variation was lower than that obtained with the sodium formate system. At short residence time (i.e.,  $\tau \approx 17$  s), the concentration of nitrophenol strongly controlled the efficiency of the system (Figure 4). The degradation efficiency decreased almost linearly from 90% to approximately 40% at a nitrophenol concentration of 350 mg NP L<sup>-1</sup> and then stabilized at a concentration of 500 mg NP L<sup>-1</sup>. There was a small decrease in the degradation efficiency with increased processing time, but the difference was not as marked as in the case of the sodium formate process. When the residence time was longer (i.e.,  $\tau \approx 32$  s), the limiting effect of substrate concentration was less drastic: the degradation efficiency progressively decreased down to 65%. Increasing the residence time decreased the influence of nitrophenol concentration on degradation efficiency. In the case of hydrogen gas, the efficiency of the process may be controlled by the permeability properties of the membranes and the pressure gradient between the inlet and outlet compartments of the cell, which in turn may affect its dissolution in the solution and therefore the reaction rate. The catalytic activities were

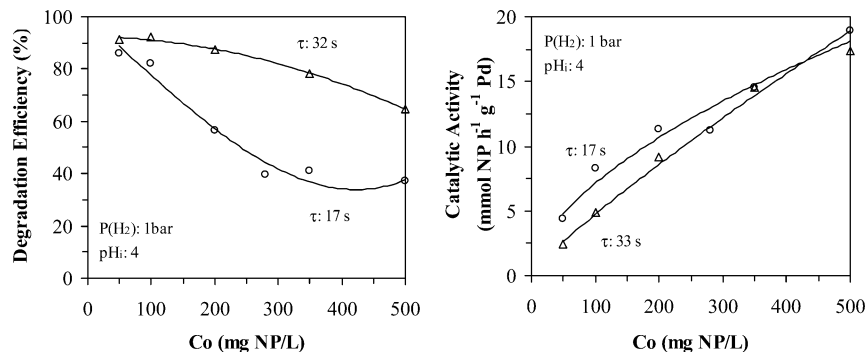


FIGURE 4. Influence of nitrophenol concentration ( $C_o$ ) on degradation efficiency (left) and catalytic activity (right) using hydrogen gas as the hydrogen donor.

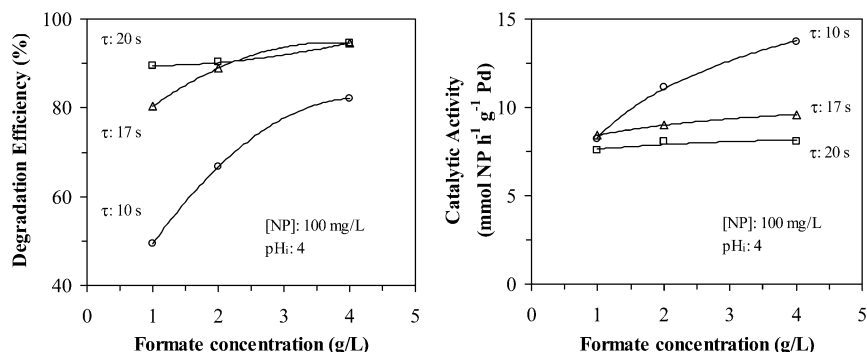


FIGURE 5. Influence of sodium formate concentration on degradation kinetics (left) and catalytic activity (right) for given mean residence times.

also determined for short and long residence time. As expected, the catalytic activity increased with increasing nitrophenol concentration. The catalytic activity was slightly higher at short residence time than at long residence time, especially at low nitrophenol concentration, while at high substrate concentration the catalytic activities tended to a similar value close to  $18 \text{ mmol NP h}^{-1} \text{ g}^{-1} \text{ Pd}$  (at  $C_o$ ,  $500 \text{ mg NP L}^{-1}$ ). This value is slightly (but significantly) higher than that obtained at the same nitrophenol concentration with sodium formate as the hydrogen donor.

These results show that both the kinetic rate (controlled by the residence time of the solution in the fiber) and the excess of hydrogen donor (versus the concentration of nitrophenol) control the efficiency of the catalytic system. Sodium formate appeared to be more efficient than hydrogen gas in the degradation of nitrophenol. However, a small part of the substrate flowed through the membrane and was collected in the formate solution, giving contaminated solutions. Moreover, at high nitrophenol concentration, there was a progressive decrease of treatment efficiency as the operation went on, while in the hydrogen gas system the variation was less significant (less than 3%).

**Influence of Sodium Formate Concentration and Hydrogen Pressure.** The concentration of formate was varied (between 1 and  $4 \text{ g F L}^{-1}$ ) for different flow velocities (corresponding to different residence times,  $\tau \approx 10, 17,$  and  $20 \text{ s}$ ). As expected, increasing formate concentration increased the treatment efficiency, especially at short residence time (Figure 5, left). For a short contact time ( $\tau \approx 10 \text{ s}$ ), the degradation efficiency exceeded 80% with a  $4 \text{ g L}^{-1}$  formate solution but the curve tended to stabilize. At longer contact time, the degradation efficiency also increased with formate concentration but to a lesser extent: the degradation efficiency varied between 80% and 94%. Considering the evolution of the conversion yield during the process, it appears that it remained almost constant when formate concentration was 2 and  $4 \text{ g L}^{-1}$ , while at a formate concentration of  $1 \text{ g L}^{-1}$  at short constant time ( $\tau \approx 17 \text{ s}$  or

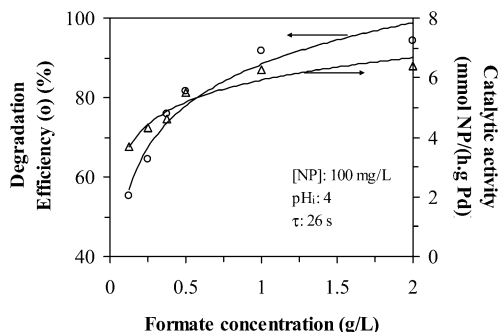


FIGURE 6. Influence of sodium formate concentration on degradation kinetics and catalytic activity for given mean residence times.

lower), a significant decrease in degradation efficiency was observed (5–9%). This is indicative of a lack of hydrogen donor, which may influence degradation kinetics. A complementary experiment was performed at long residence time ( $\tau \approx 26 \text{ s}$ ) with a larger range of formate concentration (between  $0.125$  and  $2 \text{ g L}^{-1}$ ). Figure 6 shows that below a hydrogen donor concentration of  $0.5 \text{ g L}^{-1}$ , degradation kinetics increased almost linearly with the concentration of formate solution, while above this concentration the curve had an asymptotic trend. The catalytic activity was also controlled by the formate concentration, but the effect significantly depended on the residence time (Figure 5, right). The most significant differences were obtained at low residence time, for which the catalytic activity was obviously higher. At lower contact time, the influence of sodium formate concentration increased. The catalytic activity tended to stabilize, at high formate concentration, close to 15, 10, and  $8 \text{ mmol NP h}^{-1} \text{ g}^{-1} \text{ Pd}$  at  $\tau \approx 10, 17,$  and  $20 \text{ s}$ , respectively. This increase of the catalytic activity is consistent with previous results obtained with flaked catalyst particles (40,43). Figure 6 confirms these conclusions using a broader sodium formate concentration range; the catalytic activity

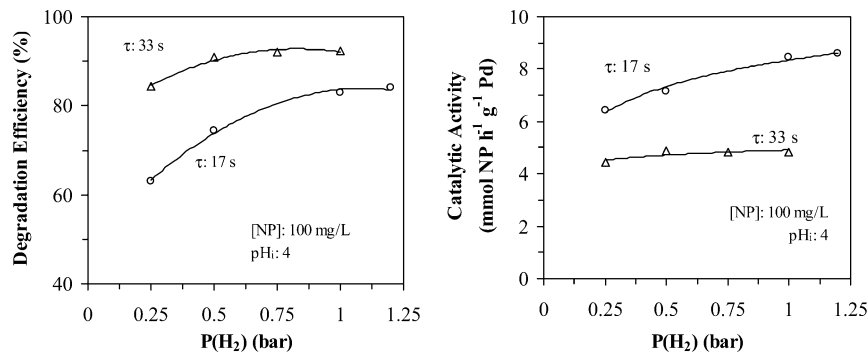


FIGURE 7. Influence of hydrogen pressure on degradation efficiency (left) and catalytic activity (right) for given mean residence times.

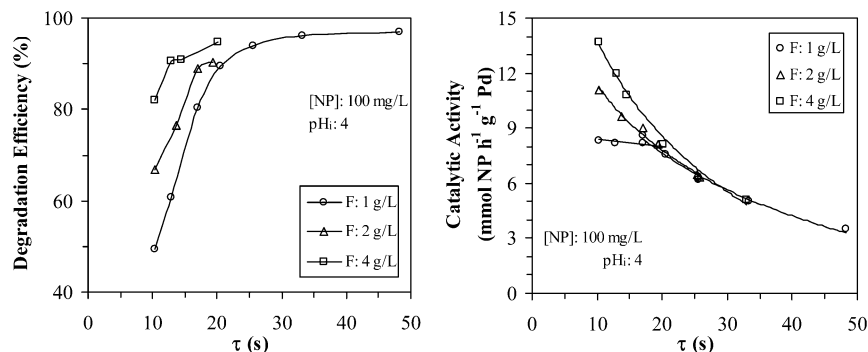


FIGURE 8. Influence of mean residence time on nitrophenol degradation kinetics (left) and catalytic activity (right) at different concentrations of sodium formate.

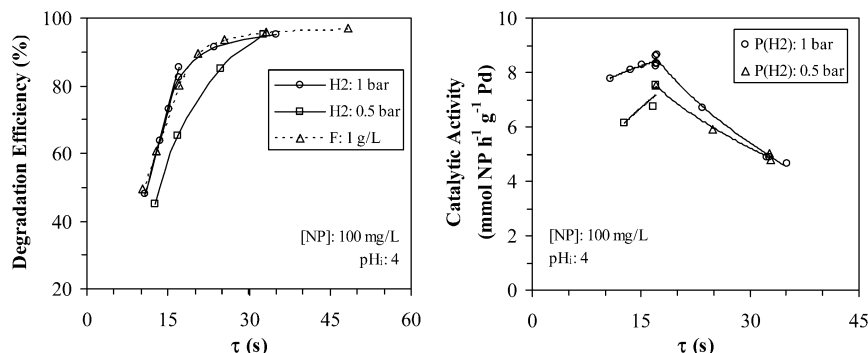


FIGURE 9. Influence of mean residence time on nitrophenol degradation efficiency (left) and catalytic activity (right) at different hydrogen pressures.

increases asymptotically (up to a  $6.7 \text{ mmol NP h}^{-1} \text{ g}^{-1} \text{ Pd}$  value) under selected experimental conditions (NP concentration,  $100 \text{ mg L}^{-1}$ ;  $\tau \approx 26 \text{ s}$ ). Above a sodium formate concentration of  $1 \text{ g L}^{-1}$ , the increase in degradation efficiency and catalytic activity was negligible.

In the case where hydrogen gas was used as the hydrogen donor, as expected, increasing the gas pressure increased degradation efficiency (Figure 7, left). However, the improvement in the conversion yield was also very sensitive to the residence time. At short residence time, the conversion yield increased by 20% when hydrogen pressure was increased from 0.25 to 1 bar. At increased residence time (up to  $\tau \approx 33 \text{ s}$ ), the conversion yield significantly increased above 84%. However, the effect was significantly less sensitive: the improvement in degradation efficiency did not exceed a few percent when hydrogen pressure was increased from 0.5 to 1 bar. Increasing contact time decreased the influence of hydrogen pressure. The gradient in hydrogen pressure controls hydrogen dissolution in water, which in turn may control reaction kinetics. It is also important to observe that, with hydrogen gas, the decrease in the conversion yield was not observed during the course of the operation, as occurred with sodium formate. The degradation efficiency was sig-

nificantly more stable with the hydrogen gas system compared to the system using sodium formate as hydrogen donor. It is interesting to observe in Figure 7 (right) that increasing hydrogen pressure had a very limited effect on the catalytic activity at long residence time. At low residence time, increasing the hydrogen pressure significantly increased the catalytic activity, which remained higher than that obtained at long contact time.

Using hydrogen gas reduces the production of secondary contaminated flows (such as those occurring by transfer of nitrophenol through the membrane into the sodium formate solution outer surface of the fiber). Experimental conditions are expected to be easier to control when using this hydrogen donor. Moreover, using hydrogen gas as the hydrogen donor avoids introducing an additional contaminant (unreacted sodium formate) into the treated solution.

**Influence of Residence Time.** The preceding sections have clearly identified the residence time as an important criterion for the design of the treatment unit. The influence of the residence time on degradation kinetics was therefore investigated more deeply with different experimental conditions using both sodium formate (Figure 8) and hydrogen gas as hydrogen donor (Figure 9).

Increasing the residence time allowed the efficiency of nitrophenol degradation to be improved, especially at short contact time (Figure 8, left). Hence, at short contact time the degradation efficiency linearly increased with the residence time up to a limit contact time for which the conversion yield stabilized and tended to an asymptotic value, around 95%. In the case of a formate solution used as hydrogen donor, increasing sodium formate concentration decreased the residence time required to reach degradation efficiency higher than 90%: 12 s at 4 g L<sup>-1</sup>, 15 s at 2 g L<sup>-1</sup>, and 20 s at 1 g L<sup>-1</sup>. Increasing the concentration of formate in the hydrogen-donor compartment may enhance its transfer through the hollow fiber membrane. When the flow velocity is low (corresponding to long residence time) there was enough time for formate to diffuse and react at the surface of the catalyst to degrade the nitrophenol. When the residence time decreased, the slow velocity of the degradation reaction was additionally limited by the lack of hydrogen donor and it was necessary to increase the concentration of sodium formate to increase the efficiency of the system. Now considering the catalytic activity, shown in Figure 8 (right), obviously it decreased with increasing residence time, especially with high formate concentration. Above a residence time of 15–17 s, the curves obtained at three different formate concentrations overlapped, showing that it is not necessary to increase formate concentration at long residence time. At low formate concentration the catalytic activity hardly varied at low residence time and began to decrease when the residence time exceeded 17 s.

As with the sodium formate system, when hydrogen gas was used as the hydrogen donor the degradation efficiency strongly increased when the residence time was increased up to a limit residence time which depended on hydrogen pressure. Above this limit residence time, the degradation efficiency increased asymptotically with a maximum degradation efficiency that did not exceed 95%. The limit residence time decreased slightly when the hydrogen pressure was increased. It is interesting to observe that the curve at 1 bar hydrogen pressure perfectly overlapped the curve obtained with a sodium formate concentration of 1 g L<sup>-1</sup>. These experimental conditions correspond to the equivalence point for the different systems. The catalytic activity was also slightly influenced by hydrogen pressure. However, the difference between 0.5 and 1 bar was not very marked, especially at high residence time. The shape of the catalytic activity curve was different from those obtained with the sodium formate system: the catalytic capacity reached a maximum close to a residence time of 15–17 s. In this case again the catalytic activities were 2-fold lower for the hydrogen gas system compared with the sodium formate solution.

The residence time is a key parameter for the process. However, optimization of the process requires that the concentration of the hydrogen donor be taken into account, since increasing its concentration reduces the minimum residence time needed to reach a fixed level of nitrophenol degradation (for example 90%). Comparing the catalytic activity for each system leads to the conclusion that the sodium formate system is more efficient for nitrophenol degradation. However, taking into account the other advantages of the hydrogen gas system, the question remains open and the final selection may be subject to complementary experiments to be performed using a different experimental setup. It would be interesting to check the efficiency of a system involving a very short residence time but with significant recycling of the solution. An increase in the efficiency of the system would be expected.

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