

Chitosan-supported palladium catalyst. IV. Influence of temperature on nitrophenol degradation and thermodynamic parameters

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Abstract

Glutaraldehyde cross-linked chitosan was loaded with palladium and then reduced using an in situ hydrogen generation procedure (Zn in sulfuric acid solution) to prepare a chitosan-supported palladium catalyst. This catalyst was successfully used to degrade nitrophenol in dilute solutions in the presence of sodium formate as the hydrogen donor. The influence of the initial concentration of nitrophenol and sodium formate was studied in order to determine the minimum molar ratio between these compounds required to achieve complete conversion of the nitrogenous product at two temperatures. Increasing the temperature decreased the excess of hydrogen donor required for complete conversion of nitrophenol. The temperature was also varied between 10 and 60 °C in order to determine the activation energy. The pseudo first-order equation was shown to fit degradation kinetics in most cases; however, for some cases it was necessary to use a variable-order equation to model the kinetics.

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1. Introduction

Phenol and its derivatives constitute an important class of water pollutants because of their stability and solubility in water. More particularly, nitrophenols and their derivatives result from the production processes of pesticides, herbicides, insecticides and synthetic dyes; they also occur in pharmaceutical and petrochemical industries. As a result, law strictly controls the discharge of wastewaters containing such organic compounds and there are stringent regulations concerning limits to their concentration in food and water. Nitrophenols are some of the most refractory pollutants that can occur in industrial wastewaters and the United States Environmental Protection Agency lists nitrophenols among the top 114 organic pollutants.

Adsorption remains the most frequently used technique for the treatment of this refractory pollution (Gupta et al., 2000; Li et al., 2001; Chern and Chien, 2002; Trochimczuk et al., 2002). The cost of these adsorbents has prompted research focused on cheap and easily obtainable unconventional adsorbents, such as charred saw-dust (Dutta et al.,

2001), or clinoptilolite (Sismanoglu and Pura, 2001). However, a major disadvantage of these sorption processes is the difficulty of recycling the sorbent after saturation. Another drawback is the production of toxic sludges. The technique actually consists of a one-way transfer of the pollutant from a disperse medium to a concentrated phase. Complete decomposition of the pollutant would be more environmentally friendly. For this reason several alternative processes for achieving partial or complete degradation of nitrophenol compounds have been studied, including photochemical oxidation (Kiwi et al., 1996; Chen and Ray, 1998; Wang et al., 1998; Andreozzi et al., 2000; Lea and Adesina, 2001); chemical oxidation (Adams et al., 1997; Goi and Trapido, 2002); and biological degradation (Arcangeli and Arvin, 1995).

Many studies have also focused on the use of catalytic processes for the degradation of nitrophenol (Pintar and Levec, 1994; Choudhary et al., 1998; Pradhan et al., 2002). Though catalytic processes may be performed in homogeneous systems, in the case of expensive catalysts such as those involving precious and strategic metals, it is important to recover the metals at the end of the process. For this reason supported catalysis has been extensively investigated in the last few decades (Baiker, 1997; Blaser et al., 2001;

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Ford, 2001). Activated carbon, alumina, and silica gel are the most used supports (Zhang and Chuang, 1998; Khilnani and Chandalia, 2001; Macquarrie et al., 2001). However, polymeric supports have recently attracted considerable attention both for their versatile conditioning and also for the forms of selectivity they can bring to the reaction (Patel and Ram, 1998; Altava et al., 2001). Indeed, these polymers, due to their stereo-specificity, can present selective separation properties, some of which have been used for the separation of enantiomers (Malinowska and Rózyło, 1997; Felix, 2001; Haginaka, 2001; Yashima, 2001). Moreover, the interactions between the metal and the polymer contribute to stabilizing the metal on the catalyst by preventing metal leaching. Many studies have recently focused on using natural polymers as support for catalyst preparation (Quignard, 2002). For example, recent studies have dealt with chitosan for the manufacturing of new catalytic systems (Chiessi and Pispisa, 1994; Jin et al., 1994; Han et al., 1996; Zeng et al., 1997; Yin et al., 1999; Quignard et al., 2000). This amino-polysaccharide is characterized by its high affinity for metal ions, which can be adsorbed either by an ion exchange mechanism (metal anions in acidic solutions) (Inoue, 1998; Guibal et al., 1999, 2000; Guzman et al., 2002), or by chelation mechanisms (metal cations in near-neutral solutions) (Kawamura et al., 1993; Guibal et al., 1995; Inoue, 1998; Bassi et al., 2000). Sorption capacities as high as $2\text{--}3\text{ mmol Me g}^{-1}$ are commonly reached with gold, platinum and palladium, under mild experimental conditions (Guibal et al., 1999; Ruiz et al., 2000). The reduction of loaded metals by a suitable procedure (using sodium borohydride and/or in situ generated hydrogen) allows loaded metals to be present on the support at the zero-valent oxidation state, which is appropriate for many hydrogenation procedures (Vincent and Guibal, 2002). This kind of catalyst has been investigated for chromate reduction using sodium formate as the electron donor: chromate reduction may result from hydrogen transfer mechanism and/or by production of hydrogen from formic acid oxidation (Vincent and Guibal, 2002). This support has also been used for chlorophenol dehalogenation under similar experimental conditions, using sodium formate as the hydrogen donor (Vincent et al., 2003). Previous work focused on studying the influence of experimental parameters: pH, catalyst dosage, catalyst particle size, catalyst loading, sodium formate concentration and nitrophenol concentration at room temperature on the degradation of nitrophenols using sodium formate as the hydrogen donor (Vincent and Guibal, 2003). The products of nitrophenol degradation were identified by mass-spectrometry coupled with gas chromatography and by high pressure liquid chromatography. Nitrophenol was degraded into intermediary products such as aminophenol. After a long contact time, after disappearance of formate aminophenols are oxidized; however, the final products strongly depend on experimental conditions (type of nitrophenol, oxidation conditions, etc.)

(unpublished results). This preliminary investigation (and more specifically the study of effect of particle size and catalyst dosage on degradation kinetics) showed that most of the reaction was limited to the external surface of the catalyst and that the internal part of the particle did not contribute to the degradation (Vincent and Guibal, 2003).

The present study investigates the influence of temperature on the reaction kinetics at varying formate and 3-nitrophenol (3-NP) concentrations. The energetic parameters of the system were studied and the activation energy was calculated using the Arrhenius law. Degradation kinetics were modeled using several models such as a pseudo first-order kinetic equation, variable-order equation and also in some particular cases a 'reversible' reaction equation. The variation of the kinetic coefficients with experimental parameters was considered.

2. Material and methods

2.1. Materials

Chitosan was supplied by Aber Technologies (Plouvien, France). It had previously been characterized: the degree of deacetylation was 87% and the molecular weight was $125.000\text{ g mol}^{-1}$. The chitosan was ground and sieved in order to collect the $0\text{--}125\text{ }\mu\text{m}$ fraction.

NaBH_4 was purchased from Fluka (Switzerland) as an analytical grade product. PdCl_2 was purchased from Acros (USA). Other reagents (acids, zinc, HCOONa) were supplied by Carlo Erba (Italy). 3-nitrophenol (3-NP) was supplied by Fluka (Switzerland).

2.2. Catalyst preparation

The preparation of the catalyst consisted of three steps: (a) the pre-conditioning of the polymer to avoid chitosan dissolving in acidic solutions; (b) metal sorption for palladium immobilization; and (c) chitosan reduction.

Since chitosan is soluble in hydrochloric acid it cannot be used as supplied, and a cross-linking treatment is required. The procedure used for chitosan cross-linking was previously described (Vincent and Guibal, 2003). It consisted of contact of chitosan powder with glutaraldehyde solution (10% v/v) in order to maintain a 1:1 ratio between amine groups of chitosan and aldehyde functions of the cross-linking agent.

The sorbent (1 g) was mixed for 24 h with a palladium solution (2 l) at the concentration of 200 mg Pd l^{-1} at pH 2 for palladium impregnation. The reduction treatment consisted of bringing the loaded sorbent (200 mg) into contact with 100 ml of sulfuric acid solution (1% w/w) 300 mg of zinc (provided as a fine powder). A digestion/mineralization procedure (contact of the catalyst with a hydrochloric acid and hydrogen peroxide mixture) was used to disrupt the polymer and dissolve the metal. ICP analysis

confirmed the actual palladium content: 102 mg Pd g⁻¹ catalyst.

Previous studies of palladium and platinum sorption on chitosan derivatives have shown by SEM–EDAX (scanning electron microscopy coupled with energy dispersive analysis through X-ray) spectroscopy that the metals were homogeneously distributed throughout the mass of the catalyst. Transmission electron microscopy (TEM) was used to measure the size of Pd nodules or crystals. TEM observations showed that the size of metal crystals was close to 4–5 nm. The size of metal crystals is a critical parameter for catalytic activity: the smaller the size of catalyst crystals, the greater the catalytic activity (Mabbett et al., 2001). The particles were highly dispersed in the material though a slight gradient was observed between the center and the periphery of the particles. Some aggregates were also observed: the agglomeration of small nodules led to the formation of large palladium particles (around 30 nm).

X-ray photoelectron spectroscopy analysis was also performed in order to determine the oxidation state of palladium on the catalyst. It was shown that only 50–60% of palladium was reduced from Pd(II) to Pd(0).

2.3. Procedure for nitrophenol degradation

Nitrophenol degradation was performed, unless specified, by contact of 50 ml of a nitrophenol solution, containing the organic compound at a concentration of 50 mg l⁻¹ (0.36 mM) with sodium formate at a concentration of 25 mM, with 10 mg of catalyst. The pH was initially controlled at pH 3 (unless specified) using a molar sulfuric acid solution. Samples were collected at selected contact times and filtered. The filtrates were analyzed using a UV spectrophotometer (Varian 2050) and measuring the absorbance of the solutions at 332 nm, after the sample (1 ml, volume) had been acidified with 20 µl of sulfuric acid solution (5% w/w). Experiments were performed in closed vessels to avoid the stripping of the solute that may occur at high relative temperature.

Test experiments were performed (in the absence of catalyst or hydrogen donor) to check the actual influence of catalyst and hydrogen donor, and verify for reactions at high relative temperature that this parameter was not sufficient to accelerate the reaction.

2.4. Determination of kinetic parameters

The half-time reaction ($t_{1/2}$) was systematically determined to compare the times required to halve the initial concentration of nitrophenol. In addition, three other parameters were determined: (a) the catalytic activity (mmol nitrophenol min⁻¹ g⁻¹ Pd), (b) the initial rate constant (k_0 , min⁻¹), and (c) the overall rate constant (k , min⁻¹). The catalytic activity (CA, mmol 3-NP min⁻¹ g⁻¹ Pd) was obtained by determining the amount of nitrophenol transformed in a given contact time (2 min) divided by the time and the actual mass of Pd contained in the catalyst.

Three kinetic equations were used for the determination of kinetic parameters using the Langmuir–Hinshelwood kinetic model (L–H model). A more detailed discussion of these equations can be found in Schüth and Reinhard (1998) and Vincent and Guibal (2003). These equations are summarized in Table 1. Coefficients were determined by a non-linear regression analysis using the Levenberg–Marquardt algorithm included in the Mathematica[®] software application.

3. Results and discussion

3.1. Influence of molar ratio formate/nitrophenol on degradation yield

The excess of the hydrogen donor (sodium formate) versus nitrophenol concentration was varied in order to determine the minimum excess required to achieve the complete degradation of 3-NP. Table 2 and Table 3 summarize the results obtained with different formate concentrations, varying the concentration of 3-NP, at

Table 1
Summary of kinetic equations used for the modeling of degradation kinetics (Schüth and Reinhardt, 1998; Vincent and Guibal, 2003)

Model	Equation	Modeling
Pseudo first-order kinetic	$\frac{dC(t)}{dt} = -k_0 C(t)$	$\ln \left[\frac{C(t)}{C_0} \right] = -k_0 t$
Variable-order kinetic	$\frac{dC(t)}{dt} = \frac{-k_1 C(t)}{1 + k_2 C(t)}$	$t = \frac{1}{k_1} \left[\ln \left[\frac{C_0}{C(t)} \right] + k_2 (C_0 - C(t)) \right]$
Reversible kinetic	$\frac{dC(t)}{dt} = \frac{-k_1 (C(t) - C_{eq})}{1 + k_2 C(t)}$	$t = \frac{1}{k_1} \left[\left((1 + k_2 C_{eq}) \ln \left[\frac{C_0 - C_{eq}}{C(t) - C_{eq}} \right] \right) + k_2 (C_0 - C(t)) \right]$

k_0 (min⁻¹), k_1 (min⁻¹), k_2 (l mg⁻¹): kinetic coefficients; C_{eq} (mg l⁻¹): residual equilibrium concentration (case of reversible kinetic model).

Table 2

Influence of 3-NP concentration (mg l^{-1}) and sodium formate concentration (mM) on kinetic parameters for 3-NP degradation by a chitosan-supported palladium catalyst (T : 22 °C)

3-NP	F	$t_{1/2}$ (min)	k_1 10^2 (min^{-1})	k_2 10^3 (l mg^{-1})	Time range (min)	k_0 10^2 (min^{-1})	CA ($\text{mmol min}^{-1} \text{g}^{-1} \text{Pd}$)	Yield (%)
200	6.25	105	2.2*	0.13*	0–40	0.6	0.48	≈ 56
100	6.25	41	3.6*	10.2*	0–150	1.3	0.49	≈ 89
50	6.25	14	13.0	43.5	0–40	3.8	0.80	> 97
100	3.13	NS	NS	NS	NS	0.8	0.28	≈ 34
50	3.13	56	3.0*	0.41*	0–75	1.2	0.47	≈ 60
25	3.13	NS	NS	NS	NS	1.0	0.09	≈ 62
50	1.56	NS	NS	NS	NS	NS	0.31	< 10
25	1.56	NS	NS	NS	NS	NS	0.13	≈ 15

Kinetic parameters marked with an asterisk were obtained using the reversible reaction equation. NS, non-significant modeling.

the temperatures 22 and 60 °C, respectively. At low temperature and low formate concentration, increasing 3-NP concentration resulted in a decrease in both the degradation rate and the equilibrium concentration of the substrate (Table 2) (Vincent and Guibal, 2003). Under these experimental conditions, the excess of formate was not sufficient to completely degrade 3-NP. Table 3 shows that when the temperature was increased to 60 °C, for similar formate and 3-NP concentrations (i.e. formate: 6.25 mM and 3-NP: 50–100–200 mg l^{-1}), the degradation yield was significantly higher: up to 84% at the highest concentration and complete below a nitrophenol concentration of 200 mg l^{-1} . Increasing formate concentration resulted in a complete degradation of 3-NP, though, as expected, increasing the concentration of 3-NP slightly decreased its degradation rate.

Increasing the excess of formate increased the 3-NP degradation percentage. However, the effect of this excess strongly depended on the initial concentration of formate. The positive effect of formate excess was very sensitive at low $F/3\text{-NP}$, between 4 and 9, while above 9 the increase of the degradation was less significant. It seems that a 10-fold excess of formate (compared to 3-NP concentration) was sufficient to obtain maximum nitrophenol elimination. However, increasing the temperature enhanced the effect of formate and resulted in significantly increased degradation kinetics and conversion yields under comparable experimental conditions. Similar conclusions can be reached considering the rate constant in the first moment of the reaction (k_0 in Tables 2 and 3). Standard conditions

for further experiments were established using a 3-NP concentration of 50 mg l^{-1} and a sodium formate concentration of 25 mM, though less favorable experimental conditions were used, on occasions, to measure the impact of other experimental parameters.

3.2. Influence of temperature

Catalytic processes are very sensitive to the reaction temperature. Gallezot et al. (1996) showed that the catalytic oxidation of formic acid is significantly improved by increasing the temperature: the time for half reaction was decreased 3 times from 25 to 35 °C and it was halved from 35 to 53 °C. Experiments were performed at different temperatures ranging between 10 and 60 °C, for two different sorbent dosages (50 and 200 mg l^{-1}). Increasing the temperature increased the degradation rate (Fig. 1). Tables 4 and 5 summarize the kinetic data. The time for half reaction strongly decreased with increasing temperature, especially between 10 and 30 °C. The catalytic activity followed a similar increasing trend at low temperatures, followed by stabilization at high temperature. A temperature of 40–50 °C appeared to be a good compromise. The overall rate constant was multiplied by 5 between 10 and 60 °C, independently of catalyst dosage. There was less variation in the rate constant in the initial stage of the reaction (k_0 was multiplied by 3–3.5).

The determination of kinetic rates for different experimental conditions (changing the catalyst dosage and the concentration of sodium formate) allowed the energy of

Table 3

Influence of 3-NP concentration (mg l^{-1}) and sodium formate concentration (mM) on kinetic parameters for 3-NP degradation by a chitosan-supported palladium catalyst (T : 60 °C)

3-NP	F	$t_{1/2}$ (min)	k_1 10^2 (min^{-1})	k_2 10^3 (l mg^{-1})	Time range (min)	k_0 10^2 (min^{-1})	CA ($\text{mmol min}^{-1} \text{g}^{-1} \text{Pd}$)	Yield (%)
200	25	6.5	26.8*	7.3*	0–30	7.4	2.97	≈ 96
100	25	5	15.9	–	0–20	14.4	4.98	> 97
50	25	3	28.5	–	0–13	20.0	2.90	> 97
200	6.25	15	10.6*	2.1*	0–40	1.9	1.27	≈ 84
100	6.25	14	19.9	11.3	0–26	13.2	4.05	> 97
50	6.25	4	24.2	–	0–15	23.2	3.41	> 97

Kinetic parameters marked with an asterisk have been obtained using the reversible reaction equation.

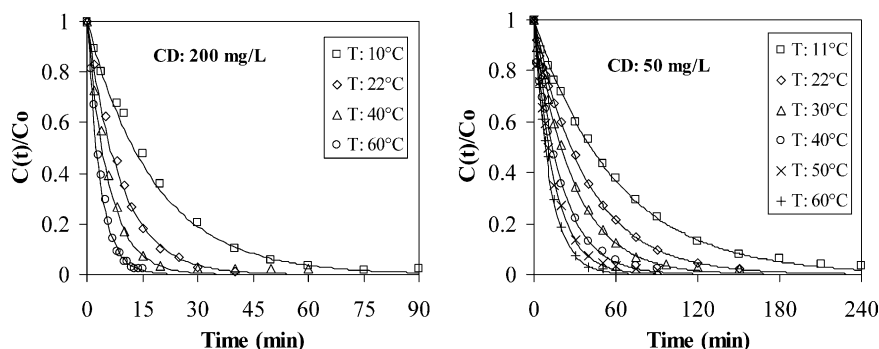


Fig. 1. Influence of temperature and catalyst dosage on 3-NP degradation kinetics.

activation to be calculated and the entropy, enthalpy, and free energy of activation to be determined.

The Arrhenius law was used to calculate the activation energy, E_a (kJ mol^{-1})

$$k = A e^{-(E_a/RT)} \quad (1)$$

where A is the pre-exponential factor (min^{-1}), T is the absolute temperature (K), and k is the rate constant (min^{-1}). The logarithm of k (respectively, k_0) was plotted versus the reciprocal of temperature and the slope of the curve was used to determine the activation energy.

The Eyring equation can also be used to determine the entropy of activation, ΔS^* ($\text{J mol}^{-1} \text{K}^{-1}$), and enthalpy of activation, ΔH^* (kJ mol^{-1}) (Sismanoglu and Pura, 2001)

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \left(\frac{\Delta S^*}{R}\right) - \left(\frac{\Delta H^*}{RT}\right) \quad (2)$$

where k_B ($1.3805 \times 10^{-23} \text{ J K}^{-1}$) and h ($6.626 \times 10^{-34} \text{ J s}$) are Boltzmann's and Planck's constants, respectively. The entropy and enthalpy of activation were obtained by plotting $-\ln k/T$ versus the reciprocal of temperature and using the intercept and the slope of the linear plots, respectively.

The free energy of activation, ΔG^* (kJ mol^{-1}) was obtained by:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (3)$$

Fig. 2 shows the linearization of these equations for experiments performed at catalyst dosages of 50 and 200 mg l^{-1} , for both the overall kinetic parameters and the initial degradation rate. Quite good correlations between experimental data and modeled curves were obtained, and thermodynamic parameters were determined (Table 6). The thermodynamic parameters were independent of catalyst dosage: the parameters varied by less than 10%. However, it is interesting to observe that they depended on the kinetic parameters used for the calculation (k_0 or k_1): with the rate constant in the first moment of the reaction, the thermodynamic constants were systematically lower than those obtained using the overall kinetic rate. The activation energy, E_a , was low, between 17 and 26 kJ mol^{-1} (depending on the calculation criteria and the catalyst dosage), indicating that the catalyst is very efficient at degrading 3-nitrophenol in the presence of sodium formate. This is consistent with the activation energy (close to 21 kJ mol^{-1})

Table 4

Influence of Temperature (T , °C) on kinetic parameters for 3-NP degradation by a chitosan-supported palladium catalyst (CD: 200 mg l^{-1} , F : 25 mM)

T	$t_{1/2}$ (min)	k_1 10^2 (min^{-1})	k_2 10^3 (l mg^{-1})	Time range (min)	k_0 10^2 (min^{-1})	CA ($\text{mmol min}^{-1} \text{g}^{-1} \text{Pd}$)
10	14	5.6	—	0–50	5.6	0.96
22	7	10.9	—	0–25	9.5	1.49
40	5	17.2	—	0–20	14.1	2.42
60	3	27.8	—	0–11	20.0	2.90

Table 5

Influence of temperature (T , °C) on kinetic parameters for 3-NP degradation by a chitosan-supported palladium catalyst (CD: 50 mg l^{-1} ; F : 25 mM)

T	$t_{1/2}$ (min)	k_1 10^2 (min^{-1})	k_2 10^3 (l mg^{-1})	Time range (min)	k_0 10^2 (min^{-1})	CA ($\text{mmol min}^{-1} \text{g}^{-1} \text{Pd}$)
11	43	1.7	—	0–150	2.5	1.76
22	28	2.6	—	0–90	3.8	2.86
30	20	3.5	—	0–75	4.7	3.80
40	13	5.1	—	0–50	5.9	6.02
50	10	6.7	—	0–40	7.0	6.11
60	9	8.6	—	0–40	7.7	5.91

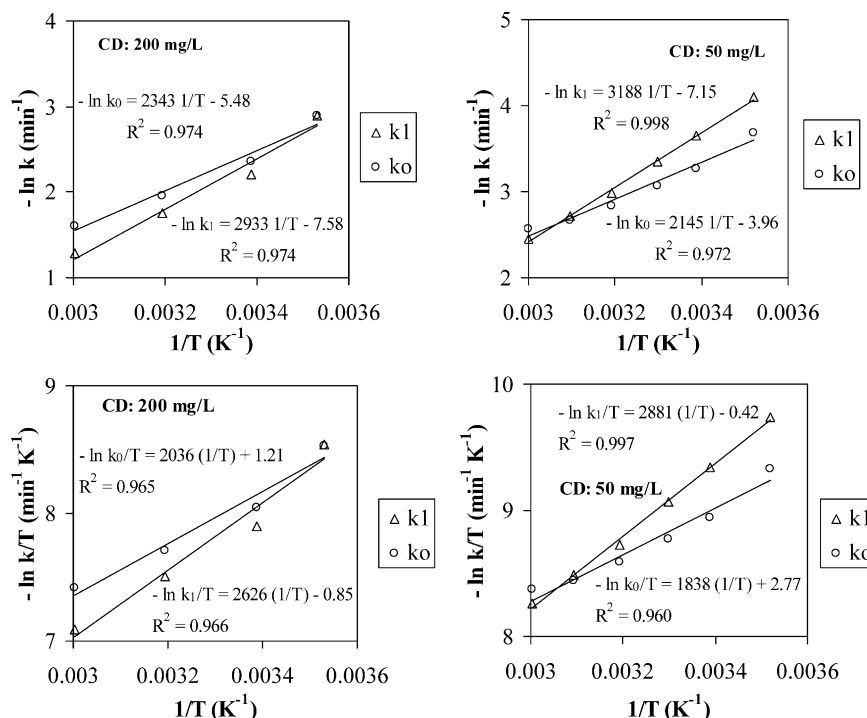


Fig. 2. Influence of temperature on the kinetic parameters of 3-NP degradation for catalyst dosages (CD) 200 and 50 mg l⁻¹—thermodynamic characteristics.

found by Vincent et al. (2003) for chlorophenol dehalogenation with the same catalyst. It is interesting to observe that this value is comparable to the activation energy calculated from data obtained by Gallezot et al. (1996) for formic acid oxidation by a platinum catalyst immobilized on activated carbon (ca. 26.4 kJ mol⁻¹). It is about 3 times higher than the activation energy found by Lea and Adesina (2001) for the oxidative degradation of 4-nitrophenol using a photocatalytic process (about 8 kJ mol⁻¹). Felis et al. (1999) found higher activation energy values for the hydrodechlorination of chlorophenol and the dearomatization of the intermediary products, using Ru/C catalysts, about 45 and 33 kJ mol⁻¹, respectively. Zhang and Chuang (1998) also found higher activation energy for the catalytic oxidation of black liquor using Pt–Pd–Ce/alumina catalyst (about 50 kJ mol⁻¹). The entropy of the system, ΔS^* , varied between –224 and –254 J mol⁻¹ K⁻¹, and the entropy was lower using the overall kinetic rate instead of the initial kinetic rate of degradation. The enthalpy of the reaction, ΔH^* , varied between 15 and 24 kJ mol⁻¹.

The concentration of formate was decreased to 6.25 mM (instead of 25 mM) and the influence of the temperature on degradation kinetics was considered with a catalyst dosage of 200 mg l⁻¹. Fig. 3 shows kinetic curves and thermodynamic curves (data from Table 5). It should be noted that the modeling of the kinetic curve at T : 22 °C required the two-parameter equation instead of the pseudo first-order equation. The thermodynamic parameters are included in Table 6. The energy of activation and the enthalpy of the reaction were significantly increased by decreasing the concentration

of the hydrogen donor, while lowering formate concentration decreased the entropy of the system.

At 22 °C, the free energy of activation, ΔG^* , varied between 87 and 91 kJ mol⁻¹, while at 60 °C, it ranged between 96 and 100 kJ mol⁻¹. These values were not altered by changing neither the catalyst dosage nor the sodium formate concentration: the variation being less than 3%.

3.3. Influence of sodium formate concentration

Though this parameter was partially investigated in the other sections, a more exhaustive study was performed under selected experimental conditions (CD: 200 mg l⁻¹, pH 3, 3-NP conc.: 50 mg l⁻¹) at two fixed temperatures 22 and 60 °C. Tables 7 and 8 summarize these data. Regardless of formate concentration, the increase in the temperature involved an increase in kinetic parameters and a decrease in

Table 6
Thermodynamic parameters

CD	F	k_0			k_1		
		E_a	ΔS^*	ΔH^*	E_a	ΔS^*	ΔH^*
200	25	19.5	–242	16.9	24.4	–224	21.8
50	25	17.8	–254	15.3	26.5	–228	23.9
200	6.25	33.9	–197	31.3	ND	ND	ND

ND, not determined since the kinetic curve was modeled using the two-parameter equation instead of the pseudo first-order equation (CD, mg l⁻¹; F , mM; E_a , kJ mol⁻¹; ΔS^* , J mol⁻¹ K⁻¹; ΔH^* , kJ mol⁻¹).

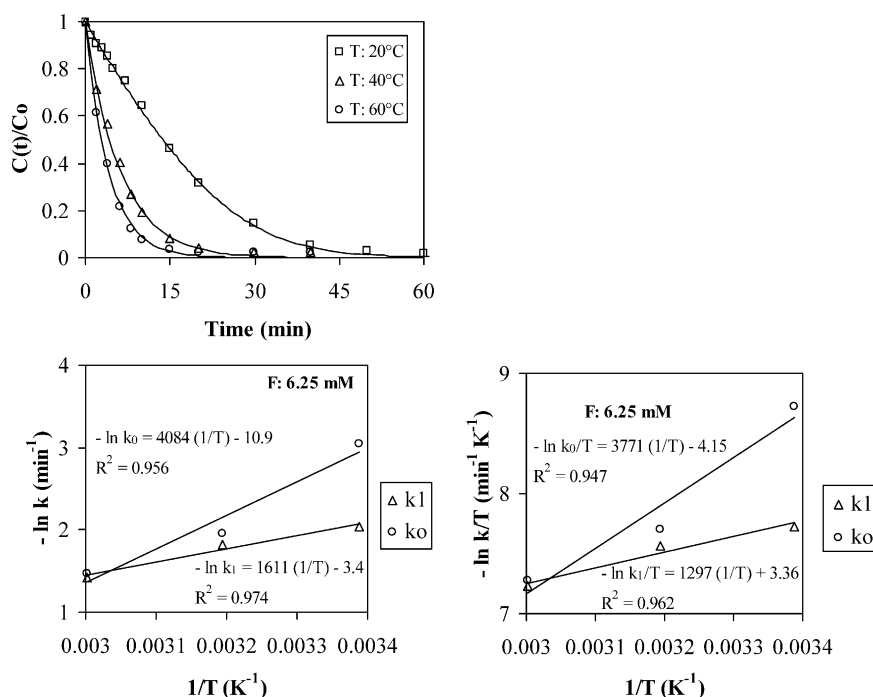
Fig. 3. Influence of temperature on 3-NP degradation kinetics at low formate concentration (F : 6.25 mM).

Table 7

Influence of formate concentration (F , mM) on kinetic parameters for 3-NP degradation by a chitosan-supported palladium catalyst at T : 22 °C (3-NP: 50 mg l⁻¹; CD: 200 mg l⁻¹)

F	$t_{1/2}$ (min)	k_1 10 ² (min ⁻¹)	k_2 10 ³ (l mg ⁻¹)	Time range (min)	k_0 10 ² (min ⁻¹)	CA (mmol min ⁻¹ g ⁻¹ Pd)	Yield (%)
50	6	11.7	—	0–30	10.8	1.99	>97
37.5	7	11.3	—	0–30	9.1	1.65	>97
25	7	10.9	—	0–25	9.5	1.49	>97
12.5	9	9.4	—	0–30	7.4	1.41	>97
9.37	10	13.2	23.9	0–40	5.5	0.97	>97
6.25	14	13.0	43.5	0–40	3.8	0.80	>97
3.13	56	3.0*	0.41*	0–75	2.7	0.47	≈60
1.56	NS	NS	NS	NS	NS	0.34	<10
0.78	NS	NS	NS	NS	NS	0.39	<10

Kinetic parameters marked with an asterisk were obtained using the reversible reaction equation. NS, non-significant modeling.

the time required to achieve the complete conversion of nitrophenol or to reach the degradation equilibrium. This is consistent with the section focusing on the influence of $F/3$ -NP ratio.

Decreasing formate concentration resulted in a decrease in the kinetic parameters k_0 , k_1 and CA, while the half-reaction time was increased. The decrease in the catalytic activity was especially significant below 12.5 mM; while

Table 8

Influence of formate concentration (F , mM) on kinetic parameters for 3-NP degradation by a chitosan-supported palladium catalyst at T : 60 °C (3-NP: 50 mg l⁻¹; CD: 200 mg l⁻¹)

F	$t_{1/2}$ (min)	k_1 10 ² (min ⁻¹)	k_2 10 ³ (l mg ⁻¹)	Time range (min)	k_0 10 ² (min ⁻¹)	CA (mmol min ⁻¹ g ⁻¹ Pd)	Yield (%)
25	3	27.8	—	0–13	20.0	2.90	>97
9.37	4	23.2	—	0–15	16.3	2.96	>97
6.25	4	24.2	—	0–15	23.2	3.41	>97
3.13	4	22.4	6.8	0–15	16.0	2.27	≈95
1.56	NS	19.9*	5.8*	0–10	2.9	0.34	≈23
0.78	NS	NS	NS	NS	NS	0.44	<10

Kinetic parameters marked with an asterisk were obtained using the reversible reaction equation. NS, non-significant modeling.

above this concentration the catalytic activity decreased only slightly. The influence of this parameter was less significant at $T : 60\text{ }^{\circ}\text{C}$. Indeed, the CAC varied with no clear tendency above $F : 3.13\text{ mM}$ and strongly decreased below this value. As stated in Section 3.1, at low temperature, formate concentration has to be 10-times higher than substrate concentration and the excess of formate required to reach the optimum degradation of 3-NP is lowered at high temperature. This is consistent with the calculation of thermodynamic constants where the activation energy was found to significantly increase with decreasing formate concentration.

4. Conclusion

Chitosan appears to be a very efficient support for palladium in order to prepare a catalyst for the degradation of nitrophenols into aminophenol using sodium formate as the hydrogen donor. Two reactions may be involved: direct hydrogen transfer from the hydrogen donor or degradation of sodium formate and production of hydrogen, which finally reacts with nitrophenol. The reaction appears to be more efficient in acidic solutions: initial pH below pH 4–5 appears to be an optimum, though the pH strongly increased during catalytic degradation, possibly due to formate degradation into CO_2 . A large excess (about 10-fold) of sodium formate compared to nitrophenol is required to reach the maximum degradation for a given substrate concentration. This required excess decreases with increasing reaction temperature. The temperature strongly affects degradation rates: increasing the reaction temperature, especially between 10 and $40\text{--}50\text{ }^{\circ}\text{C}$, strongly increases catalytic efficiency and kinetics. The energy of activation was calculated for different experimental conditions and it was found to be between $18\text{ and }26\text{ kJ mol}^{-1}$, depending on the catalyst dosage and calculation procedure (kinetic parameter— k_0 or k_1 —used in the Arrhenius plot). The low values of activation energy show that the chitosan-supported Pd-catalyst is very efficient at degrading nitrophenol. Similar experiments were performed under less favorable conditions (ca. lower formate concentration) and the energy of activation was found to increase up to 34 kJ mol^{-1} .

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