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Research Article

Reductive Degradation of Polychlorinated Phenols by Pd/C-Formate: An Ecoefficient Remediation Method for Aqueous Chlorinated Phenols

A new catalytic dehydrohalogenation method for chlorinated phenols is described, which can be used to break down chlorinated pollutants in wastewater. It uses a system of Pd-C as catalyst with sodium formate as reducing agent. This economic method is easy to perform with a complete degradation of the pollutant within 12 to 30 h at room temperature. The ecoefficiency of the procedure is compared with eleven alternative methods showing the special advantages of the method.

Keywords: Chlorophenols; Remediation; Wastewater

Received: February 16, 2007; *revised:* April 16, 2007; *accepted:* April 24, 2007

DOI: 10.1002/clen.200700021

1 Introduction

Chlorophenols have been used in pesticides, disinfectants, wood preservatives, personal care formulations, and many other technical products. They are also substantial by-products of the wood pulp bleaching process with chlorine, where they are emitted by wastewaters [1]. However, increasing knowledge about toxicity and environmental fate of these compounds resulted in regulation acts for production and distribution by various governments. In most European countries pentachlorophenol (PCP) has been banned as commercial fungicide; five chlorophenols are listed by the U.S. Environmental Protection Agency as priority pollutant, including PCP and 2,4,6-trichlorophenol, which occur, according to Ramamoorthy and Ramamoorthy [1], in the environment in significant quantities.

Several oxidative degradation methods exist for these classes of compounds using H₂O₂ as oxidant. A French group [2] reported most effective methods for oxidations in homogeneous solution; a recent method developed uses H₂O₂ in the presence of Fe-TAML as catalyst [3]. An alternative remediation method would be a reductive cleavage of chlorophenols yielding chloride and phenol, the latter being readily biodegradable. While there are several reductive dechlorination methods reported in the literature for aromatic chlorine compounds, most of these methods have been used for monochlorinated compounds [4–12].

It should be mentioned that there are some other procedures for hydrodechlorination of aromatic halides such as hydrodechlorination by special electrochemistry techniques [13] and treatment with iron and photolytic hydrodehalogenations [14], but these methods are not appropriate for practical remediation. PCP has been dechlorinated efficiently with a variety of metals like Ag/Fe in subcritical water at temperatures of 200 to 350 °C [15], certainly not useful

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Abbreviations: PCP, pentachlorophenol

for remediation of wastewaters. There is an extensive review article about reductive hydrodehalogenations of organic halides [16].

Here, the development of an efficient hydrodechlorination method for perchlorinated aromatic compounds in aqueous solution is described, which uses Palladium on charcoal as catalyst and sodium formate as reducing agent. The method was described recently by an Italian group, who employed it on monochlorinated arene derivatives on preparative scale [11]. We have modified the method in order to use it for chlorinated phenols and PCP at environmentally relevant levels and compared it with other existing methods according to its practical use and ecoefficiency.

2 Materials and Methods

2.1 General Survey About Substrates and Reagents

In preliminary experiments 4-chlorophenol and 2,4,6-trichlorophenol were subjected to hydrodechlorination, using an excess of sodium formate in presence of catalytic amounts of Pd/C in analogy to the described preparative method [11]. Small amounts of sodium formate were added to the reaction mixture in definite time intervals in order to keep up with the continuous catalytic disproportionation of aqueous formate into H₂ and CO₂, following the reactions using GC/MS technique (see below). After three hours of reaction time these two chlorophenols were completely (>99.9%) converted to phenol.

Following this method was used on pentachlorophenol as an example for a perchlorinated aromatic compound. It is important to add sodium formate in small quantities in appropriate time intervals to the mixture to ensure quantitative dechlorination. An optimized procedure is given below. All chlorophenols were pure compounds obtained from Sigma-Aldrich. Palladium/C with 10% Pd was a product from Merck, also sodium formate was obtained from this company. Inorganic chloride was determined by a standard method using ion chromatography [17]. For identification and quantification ¹³C-labelled standards of chlorophenol isomers (2-

chloro-; 2,4-dichloro-; 2,4,5-trichloro-; 2,3,4,5-tetrachloro-; 2,3,4,5,6-pentachlorophenol) purchased from Wellington Laboratories (Guelph, Canada) were used.

2.2 Optimized Procedure for Hydrodechlorination of Polychlorinated Phenols

A solution of 500 mg (7.35 mmol) sodium formate in 80 mL water in a 500 mL three-necked flask with gas inlet was deaerated with nitrogen. After 15 min the nitrogen flow was reduced and 5 mg of Pd/C (10%) was added. The mixture was vigorously stirred for 15 min in order to activate the catalyst. A solution of 10 mg (0.038 mmol) PCP is suspended in 10 mL water, adjusted to pH 10 by adding an aqueous solution of ammonia, followed by addition of 200 mg of sodium formate. The mixture was stirred for 8 h. Each hour 200 mg of sodium formate was added. After this time 500 mg of formate salt was added and the mixture was further stirred for 24 h. Reaction samples of 0.5 mL were taken at appropriate time intervals to follow the reaction (see Fig. 1). The samples were filtrated through a piece of cotton wad.

2.3 Instrumental Analysis

10 μ L of the filtrated sample was mixed with 10 μ L of a 13 C-labelled chlorophenol mixture dissolved in acetic anhydride. 30 μ L water and 10 μ L n-hexane were added and the mixture was shaken vigorously. After separation of the hexane phase 1 μ L of it was injected splitless into a GC/MS system, consisting of a Thermo SSQ 7000 single quadrupole mass spectrometer coupled with an Agilent 5890 Series II gas chromatograph. For chromatographic separation a Restek Rtx-5Sil MS capillary column (length: 30 m, ID: 0.25 mm, df: 0.10 μ m) was used and the following temperature program was applied: 60°C (hold 1.5 min) to 260°C @ 8°C/min. (hold 5 min). The MS was operated in SIM mode and the two most abundant masses of the molecular ion cluster were detected.

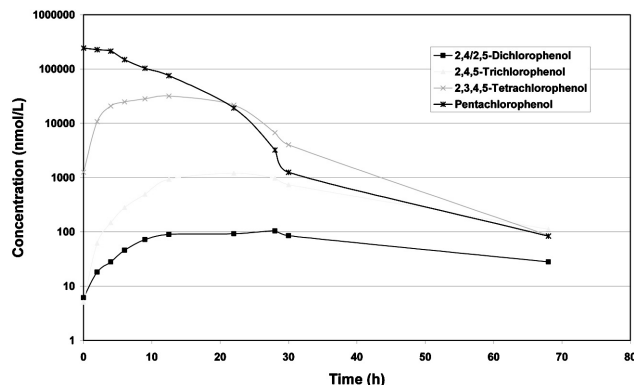


Figure 1. Reductive dechlorination of PCP to reaction intermediates.

3 Results and Discussion

The reduction works best in at least 0.01 molar solutions of sodium formate, no matter the concentration of PCP, which is usually (that is, in wastewaters) much lower than 0.01 M. A PCP concentration of 100 mg/L (0.376 mmol/L) was used for the experiments. At lower concentrations of sodium formate the reaction also works, but takes much more time. As sodium formate is very cheap, this drawback is easily compensated by the advantages of working at room temperature in an aqueous solution with an easily recyclable catalyst.

Nearly all isomers of chlorinated phenols, penta- to monochlorinated compounds can be observed, with the exceptions described below, see Tab. 1 and Fig. 1. Small quantities of phenol and non-perchlorinated phenols are detected before the addition of the reducing agent due to minor contamination of the high-purity-PCP (99%) with these derivatives.

Further a nearly equal adsorption of all chlorophenols on the activated carbon, although in fact some of them are sure to be adsorbed better than others, was assumed. So there is a certain under-determination, which affects all phenols alike and has, therefore, no influence on the relative amounts of phenols.

Table 1. Reductive dechlorination of PCP to phenol via chlorinated phenols, results from HRGC/MS.^{a)}

Time (h)	0	2	4	6	9	12.5	22	28	30	68
Phenol	5 175	83 339	139 263	216 375	302 773	610 615	966 954	1 027 266	1 075 401	1 120 115
2-Chlorophenol	38	496	1 096	640	609	811	849	2 072	1 647	1 404
3-Chlorophenol	8	139	260	404	694	1 697	1 675	2 133	1 761	273
4-Chlorophenol	8	8	8	8	8	8	8	8	8	8
2,6-Dichlorophenol	32	191	314	412	488	1 261	1 033	730	655	84
2,4/2,5-Dichlorophenol	6	18	28	46	72	90	92	104	85	28
2,3-Dichlorophenol	6	6	6	6	6	6	16	17	6	6
3,5-Dichlorophenol	27	85	157	283	440	741	931	870	707	108
3,4-Dichlorophenol	6	12	54	102	195	215	465	473	396	165
2,4,6-Trichlorophenol	5	73	101	161	172	258	226	172	127	16
2,3,6-Trichlorophenol	322	2 351	3 020	3 425	3 353	3 723	2 082	1 034	711	35
2,3,5-Trichlorophenol	60	48	105	184	311	449	302	215	146	5
2,4,5-Trichlorophenol	5	62	148	280	491	928	1 206	970	738	112
2,3,4-Trichlorophenol	140	1 539	2 688	3 680	5 008	7 252	8 185	4 319	2 895	218
3,4,5-Trichlorophenol	39	346	846	1 392	1 818	2 371	3 232	1 672	1 197	114
2,3,5,6-Tetrachlorophenol	1 032	5 410	5 648	5 639	4 716	3 084	1 860	640	459	4
2,3,4,6-Tetrachlorophenol	2 979	15 281	16 716	17 791	14 501	15 128	14 394	5 340	4 074	278
2,3,4,5-Tetrachlorophenol	1 261	10 780	20 754	24 844	28 176	31 658	21 603	6 710	4 028	86
Pentachlorophenol	242 209	227 367	212 501	149 020	103 404	75 743	19 074	3 214	1 245	83

^{a)} in (nmol/L)

Table 2. Survey of various methods of hydrodechlorination reactions of chloroaromatic compounds.

No.	1	2	3	4	5	6	7	8	9	10	11	12
Substrate	monochloro-arenes	2-chloro-toluene	monochloro-benzenes	chloro-benzene	chloro-benzene	chloro-phenols	PCDD/F	Halogenated benzenes	Monochlorinated benzenes	Perchlorinated biphenyls, ethers	OCDD/F	Chlorinated phenols
Solvent	methanol	ethanol/H ₂ O	2-propanol	H ₂ O	H ₂ O	ethanol	isooctane/H ₂ O, PTC	isooctane/H ₂ O, PTC	H ₂ O	THF	THF	H ₂ O
Time [h]	0.5	0.5	1.5	5	3	2	3	3	1–5	0.5	2	50
Temperature [°C]	25, 60	25	85	25	25	35	50	50	25–100	25	25	25
Reagent	HCOONH ₄	HCOONa	HCOONa	HCOOH	H ₂ NNH ₂	H ₂ , pressure	H ₂ , 1 atm	H ₂ , 1 atm	HCOONa	C ₈ K	C ₈ K	HCOONa
Catalyst	Pd/C	Pd/C	RhCl(PPh ₃) ₃	Pd/Al ₂ O ₃	Pd/Al ₂ O ₃	Pd/C	Pt/C	Pd/C	Pd/C	none	none	Pd/C
Yield [%]	80–100	100	85, mono-dechlorin.	90	60–90	70–99	98	90–100	90–98	ca. 99	ca. 100	100
Economy (Costs)	medium	medium	high	medium	medium	high	medium	medium	low	high	high	low
(Eco)toxicity	low	low	high	medium	high	low	low	low	low	low	low	low
Complexity of Apparatus	medium	medium	medium	medium	medium	high	high	high	medium	high	high	low
Ref.	[4]	[5]	[6]	[7]	[7]	[8]	[9]	[10]	[11]	[12]	[12]	this work

In spite of this, the amount of phenol detected in the reaction mixture is somewhat higher than expected. We believe the over-determination is also slightly due to the derivatization method for GC/MS, but can not exceed the level of the initial phenol. The chloride ion concentration of a reaction mixture after 24 h was determined by ion chromatography, showing 93.6% of delivered chloride from PCP as in water dissolved ions. Results from GC-MS are depicted in Fig. 1 and Tab. 1, respectively.

3.1 Kinetics and Regioselective Behavior

The reaction $\text{Ar-Cl} + \text{HCO}_2\text{Na} \rightarrow \text{Ar-H} + \text{CO}_2 + \text{NaCl}$ seems to follow pseudo-first order kinetic behavior for degradation of PCP with a half-life $t_{1/2}$ of about 10 h.

Due to the experimental conditions, which were optimized for archiving complete degradation in a short time, no exact evidence on kinetics can be drawn from the results, since sodium formate was added in defined time intervals activating the system, but leading to special humps in the plots of Fig. 1.

Besides, some interesting phenomena about the regioselectivity of the reaction were detected by comparison of several solutions of ¹³C-labelled chlorophenols with samples of the reaction mixture in GC-MS. It was found that conversion of PCP to tetrachlorophenols prefers dechlorination in ortho- and meta-position compared to dechlorination in para-position. The next dechlorination shows high preference for the positions next to the primary dechlorination, yielding mostly 2,3,4- and 2,3,6-trichlorophenol, along with a smaller amount of 3,4,5-trichlorophenol due to dechlorination at both ortho-positions. Thus the reaction seems not to follow the usual rules for regioselectivity found in aromatic substitutions. Furthermore, 2,3-dichlorophenol and 4-chlorophenol are not found at all in the reaction mixture. We assume roughly equal reactivity for all regioisomers, so the distribution of tetra-, tri-, and dichlorophenols should only depend little on differences in reactivity of the species. Rearrangement of chlorides during the reaction seems quite unlikely, too.

Figure 2 shows the distribution of chlorophenols within each substitution degree after 6 h, found on weight% by GC-MS with ¹³C-standards.

Further investigations using theoretical calculations will be required to explain these observations.

3.2 Evaluation of the Method Towards Reaction Conditions

The reaction was performed at a pH of about 10, in slightly alkaline solution of ammonia. This was done, because chlorophenols are readily soluble at these conditions. Another group has shown that hydrodechlorination of chlorinated compounds without pH-sensitive groups by hydrogen with Pd catalysts do not depend substantially on the pH value of the solution [7]. Our results are related to laboratory setups, conditions under realistic behavior using real wastewater still have to be explored. The influence of temperature was not investigated since we are interested in an applied method run at room temperature.

3.3 Evaluation of the Present Method With Other Hydrodechlorination Procedures

In Tab. 2 this method was compared with other hydrodechlorination methods according to the choice of substrates, solvents, temperature, time, catalyst, yield, economic efficiency (costs), eco- and human toxicity, and complexity of the necessary apparatus. A critical survey of this method has been published recently [18].

4 Conclusions

A new catalytic dehydrohalogenation method for chlorinated phenols has been described, which can be used to break down chlorinated pollutants in wastewater. The efficiency of the procedure is compared with eleven alternative methods. Tab. 2 lists these twelve methods showing their specific advantages and disadvantages. Some methods are selective for certain functional groups as reported by Tundo [9].

For remediation of polychlorinated micropollutants dissolved in wastewater the present method can compete with all the other methods and can be recommended. Neither organic solvent need to

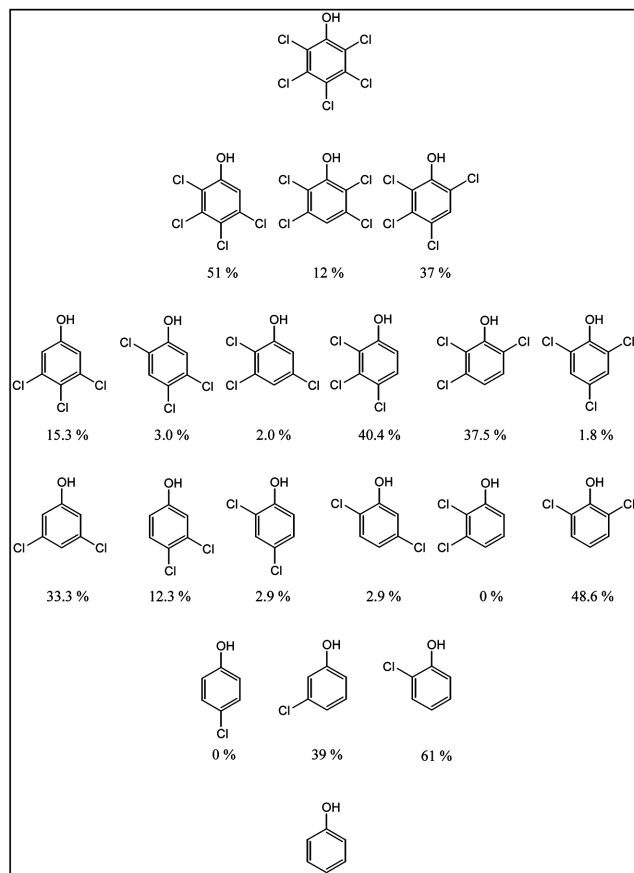


Figure 2. Distribution ratio of chlorophenol isomers and phenol after 6 h of reaction time (stirring at room temperature).

be used nor a complicated apparatus is necessary. Reaction conditions are mild: room temperature and appropriate use of a non-toxic and cheap reagent (sodium formate). The catalyst can be recycled. After treatment and filtering the catalyst, the solution can be delivered directly to municipal wastewater treatment because phenol and formate are both readily biodegradable.

There is a recent hydrodechlorination method for chlorophenols. If uses Pd/C as catalyst, but it needs high temperatures and hydrogen pressure [19].

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