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DEGRADATION OF NITROPHENOLS WITH THE FENTON REAGENT

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Abstract. The use of the Fenton reagent for degradation and detoxification of various nitrophenols (2-nitrophenol, 4-nitrophenol, 2,5-dinitrophenol, 2,6-dinitrophenol, 2-methyl-4,6-dinitrophenol, 4-methyl-2,6-dinitrophenol) was studied. The results demonstrated that nitrophenols can be successfully degraded by the Fenton reagent treatment. The optimal ratio of the chemicals was found to be hydrogen peroxide : phenol 10 : 1 and catalyst (Fe^{2+}) : phenol from 1 : 1 to 1 : 2. Further precipitation and filtration can easily remove the residual iron. According to the *Daphnia magna* acute toxicity test the Fenton treatment can lead to complete detoxification of nitrophenol solutions.

Key words: nitrophenols, Fenton reagent, degradation, toxicity assay.

INTRODUCTION

Many chemicals discharged into the aquatic environment are not only toxic but also only partly biodegradable and, therefore, not easily removed by biological treatment. Therefore there is a need to develop efficient methods for the degradation of organic pollutants into less harmful compounds or for their complete mineralization.

Nitrophenols have been used widely from the early 1930s till today as insecticides, fungicides, and herbicides. They are also used in compositions against molluscs, viruses, and helminths and as defoliants [1, 2]. The US Environmental Protection Agency has included four nitrophenols (2-nitrophenol (2-NP); 4-nitrophenol (4-NP); 2-methyl-4,6-dinitrophenol (4,6-DN-*o*-CR); and 2,4-dinitrophenol) in its 129 priority pollutants list [3]. 4,6-DN-*o*-CR, well known under the commercial name "DNOK", is a widespread insecticide [2, 4]. 2,4-Dinitrophenol is used for timber treatment [1, 3]. A product of the nitration of oil shale and coal tar phenols, nitrafen, was widely used in the USSR as an insecticide and fungicide [2]. The wastewaters from organic synthesis and manufacture of plastics, pesticides,

and dyes contain nitrophenols [1]. The degradation rate of nitrophenols is moderate in soil and quite slow on the treated plants [2]. Some insecticides, for example parathion, hydrolyze in soil with nitrophenol formation. Nitrophenols, especially mononitrophenols, are quite soluble in water, and therefore they can penetrate easily into surface and ground water.

Toxicity tests with various species and test systems demonstrated that nitrophenols are significantly more toxic than phenol (oxybenzene) [1, 5–7]. They are highly toxic upon swallowing, inhalation, and sorption through the skin [8]. Nitrophenols accumulate in the organism of warm-blooded animals. Both acute and chronic effects have been reported towards animals and humans. Epidemiological studies of mononitrophenols have indicated that they damage the central nervous system, liver, kidney, and blood.

Since 1894, when H. J. H. Fenton discovered that ferrous ion catalyzes the oxidation of malic acid by hydrogen peroxide, the combination of a ferrous salt and hydrogen peroxide, known as the Fenton reagent, has been used as one of the most effective oxidants of organic substances. Forty years later, Haber and Weiss [9] established the oxidizing species as a hydroxyl radical.

The Fenton reagent has been widely applied in the treatment of hazardous organic substances. It has the following major advantages in hazardous waste treatment technology: (1) both iron and H_2O_2 are cheap and environmentally friendly; (2) there is no mass transfer limitation due to its homogeneous catalytic nature; (3) no light is involved as catalyst and thus the reactor design is much simpler than those of UV light systems.

The classical procedure of the Fenton reagent treatment consists in the addition of hydrogen peroxide to a solution or suspension of treated compounds in the presence of ferrous ions. The reaction involves a number of steps, with the most important one shown below:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + {}^{\bullet}OH. \quad (1)$$

Hydroxyl radicals attach to aromatic or heterocyclic rings (as well as to unsaturated bonds of alkenes or alkynes). They can also abstract a hydrogen atom, initiating a radical chain oxidation:

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O, \quad (2)$$

$$R^{\bullet} + H_2O_2 \rightarrow ROH + {}^{\bullet}OH, \quad (3)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}. \quad (4)$$

The radicals produced in step (2) may undergo subsequent oxidation by ferric ions (5), reduction by ferrous ions (6), or polymerization (7):

$$R^{\bullet} + Fe^{3+} \rightarrow \text{product} + Fe^{2+}, \quad (5)$$

$$R^{\bullet} + Fe^{2+} + H^+ \rightarrow RH + Fe^{3+}, \quad (6)$$

$$2R^{\bullet} \rightarrow R—R \text{ (dimer)}. \quad (7)$$

In the 1990s considerable interest has arisen in designing water treatment systems utilizing this reaction. Several reports describing the application of the Fenton reaction for water contaminated with various organic pollutants have been published. For example, Huang et al. [10] used the Fenton reagent for the decomposition of chlorophenols. The results clearly indicate that the degradation of chlorophenols is very fast and follows a first order kinetic expression in terms of the parent compound concentration. However, only a few studies of using the Fenton reaction for the destruction of nitrophenols have been published. Lipczynska-Kochany [11] studied the degradation of aqueous nitrobenzene, 2-NP, 4-NP, and 2,4-dinitrophenol by means of photolysis in the presence of hydrogen peroxide and the Fenton (dark) reaction. A significant decomposition of pollutants was observed. Kiwi et al. [12] also compared the results of the degradation of 2-NP by means of the Fenton and photo-Fenton reagents with the result of degradation by means of photolysis in the presence of H_2O_2 at 30°C with the same conditions and initial concentrations of the reagents. The concentration of 2-NP decreased by 75% of the initial concentration over a period of 24 h [12]. Thus, for the degradation of nitrophenols the Fenton and photo-Fenton systems are more efficient than photolysis in the presence of H_2O_2. Earlier the same result was obtained by Lipczynska-Kochany [11, 13].

MATERIALS AND METHODS

The chemicals studied were 2-NP, 4-NP, 2,5-dinitrophenol (2,5-DNP), 2,6-dinitrophenol (2,6-DNP), 4,6-DN-*o*-CR, and 4-methyl-2,6-dinitrophenol (2,6-DN-*p*-CR). All chemicals, purchased from Aldrich Co, were analytical grade. The samples were prepared dissolving phenols in twice-distilled water. The rate of the degradation of nitrophenols in an aqueous solution was examined under batch conditions. The initial concentration of nitrophenols used was 0.4 mM. The pH value was 3.0, which was adjusted using 0.1 N and 1.0 N H_2SO_4.

Different concentrations of Fe^{2+} (from 0.004 to 1.0 mM/L) and H_2O_2 (from 1.0 to 10.0 mM/L) were used in these experiments. After the selected reaction time, the treated sample was taken out of the reactor for analysis of the concentration of nitrophenol. The reaction was stopped by the addition of 10% aqueous solution of Na_2SO_3. The treatment times were selected so that during the longest treatment period about 90% reduction of the initial concentration was achieved.

The concentrations of nitrophenols during the experiments were measured with a high performance liquid chromatograph (Millichrom, Nauchpribor, USSR) equipped with a UV spectrophotometer (190–360 nm). A reverse phase column,

packed with 5 μm Separon C18 (Chemapol, Czechoslovakia), was 64 mm in length and 2 mm in diameter. The isocratic method with a solvent mixture of 50% acetonitrile and 0.2% acetic acid in water with the flow rate 100 μL/min was applied. The retention times and wavelengths used in the UV detector are presented in Table 1.

Table 1. Retention times and wavelengths used in the UV detector for the analysis of nitrophenols

Nitrophenol	Retention time, min	Wavelength, nm
2-NP	3.70	280
4-NP	2.85	310
2,5-DNP	3.50	246
2,6-DNP	3.25	252
4,6-DN-*o*-CR	6.00	266
2,6-DN-*p*-CR	3.25	260

The residual concentration of hydrogen peroxide was measured spectrophotometrically (Specord UV/VIS) at 410 nm as a complex with Ti^{4+} [14].

After the treatment of the solutions with the Fenton reagent their pH values were adjusted to approximately 9.0 using 40% NaOH. In the basic medium iron ions precipitated and after that they were filtered through a paper (white ribbon) filter. Total iron residual concentration was measured in the treated and filtered solutions according to [15].

Acute toxicity of the treated nitrophenols to *Daphnia magna* (Cladocera, Crustecea) was studied. The *Daphnia* clone used was of Finnish origin (*Daphnia magna* EF) from the North Savo Regional Environmental Centre in Kuopio. Phenols were treated until at least 90% conversion of the initial compound to products was achieved. The initial concentration of nitrophenols was 0.4 mM. The living conditions were kept optimal and the 24 h toxicity test was carried out according to Finnish Standard SFS 5062 [16]. A special computer program PROBIT was used for the approximation of median effective concentration values (EC_{50}) and their 95% confidence limits.

RESULTS AND DISCUSSION

Degradation

Half-lives and 90% conversion times for the degradation of nitrophenols calculated from their degradation curves are presented in Table 2. The degradation rate was higher when higher concentrations of Fe^{2+} and H_2O_2 were used. The concentration of both hydrogen peroxide and of the catalyst Fe^{2+} affect degradation. The degradation of nitrophenols followed mainly a pseudo-first order kinetics in our experiments.

Table 2. Half-lives ($T_{1/2}$) and 90% conversion times ($T_{90\%conversion}$) for the treatment of nitrophenols with the Fenton reagent

Compound	H_2O_2 added, mM	Fe^{2+} added, mM	$T_{1/2}$, s	$T_{90\%conversion}$, s
4,6-DN-*o*-CR	10	0.01	64800	215000
4,6-DN-*o*-CR	10	0.07	1630	5430
4,6-DN-*o*-CR	10	0.1	1960	6500
4,6-DN-*o*-CR	10	0.4	218	724
4,6-DN-*o*-CR	10	0.6	<100	402
4,6-DN-*o*-CR	10	0.85	<50	224
4,6-DN-*o*-CR	10	1	<50	146
4,6-DN-*o*-CR	4	0.004	335000	–
4,6-DN-*o*-CR	4	0.4	389	1290
4,6-DN-*o*-CR	4	0.85	62	576
4,6-DN-*o*-CR	4	1	<38	355
2,6-DN-*p*-CR	4	0.4	<230	1320
2,6-DN-*p*-CR	4	0.85	<150	600
2,5-DNP	4	0.1	517	1760
2,5-DNP	4	0.4	<40	67
2,6-DNP	4	0.1	<60	1410
2,6-DNP	4	0.4	<40	413
2-NP	2	0.1	123	410
4-NP	4	0.1	225	748
4-NP	4	0.4	<30	<60
4-NP	4	1	<30	<60
4-NP	2	0.1	387	1290

– Not determined.

Table 2 shows that with increasing Fe^{2+} concentration the degradation time shortened significantly. A typical example of changes in the concentration of 4,6-DN-*o*-CR during the Fenton reaction with different concentrations of the catalyst is given in Fig. 1. When the concentration of Fe^{2+} was 0.01 mM the degradation of 4,6-DN-*o*-CR was very slow and the 90% conversion time was about 60 h. However, when the concentration of Fe^{2+} was 1 mM, the 90% conversion time was only 2.4 min. Thus, a 100-fold increase in the Fe^{2+} concentration reduced the degradation time about 1500 times. The situation was similar when the hydrogen peroxide concentration was 4 mM and different concentrations of the catalyst were applied. The pseudo-first order reaction rate constant of 4,6-DN-*o*-CR degradation calculated from its degradation curves versus the Fe^{2+} concentration is presented in Fig. 2.

The results of the present study differ from the results reported by Kiwi et al. [12], who studied the degradation of 4-NP and found that it could not be degraded faster if a higher concentration of Fe^{2+} was used. On the other hand,

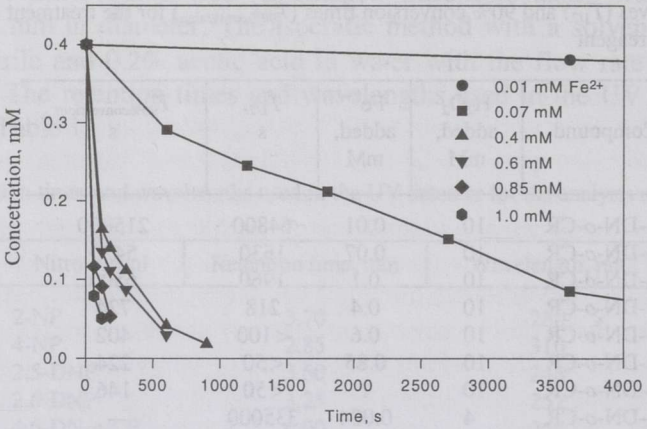

Fig. 1. Kinetics of the degradation of 4,6-DN-*o*-CR during the Fenton reaction using different concentrations of Fe^{2+} (concentration of hydrogen peroxide 10 mM).

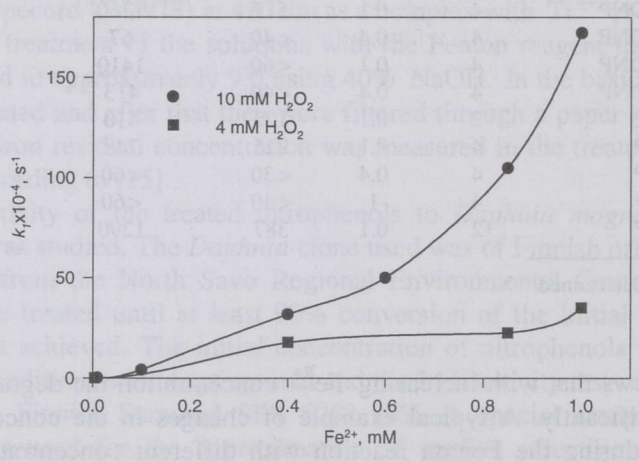

Fig. 2. Pseudo-first order reaction rate constant of 4,6-DN-*o*-CR degradation versus Fe^{2+} concentration.

Huang et al. [10], Barbeni et al. [17], and Trapido et al. [18] reported that the concentration of Fe^{2+} has a significant influence on the rate of the decomposition of various chlorophenols and substituted phenols.

The degradation rate was also affected by the concentration of hydrogen peroxide. As Fig. 2 shows the increasing of hydrogen peroxide concentration from 4 to 10 mM clearly intensifies the degradation rate of 4,6-DN-*o*-CR. For example, the pseudo-first order rate constant for 4,6-DN-*o*-CR degradation at 1 mM concentration of the catalyst and 10 mM concentration of hydrogen peroxide was

4.9 times higher than that at the same concentration of Fe^{2+} ions and 4 mM concentration of hydrogen peroxide. In a similar situation, but with the concentration of the catalyst 0.4 mM, the degradation rate was 1.8 times higher when the concentration of hydrogen peroxide was 10 mM than when it was 4 mM.

Complete degradation of all phenols under study was reached at hydrogen peroxide concentration ≥4 mM. The concentration of hydrogen peroxide equal to 4 mM can be considered as optimal for their treatment, as it enables to degrade these compounds even at lower concentrations of the catalyst within an entirely acceptable time. Complete degradation of mononitrophenols can be also reached at the Fenton reagent concentration of 2 mM H_2O_2 and 0.1 mM Fe^{2+}.

Lower concentrations of hydrogen peroxide (<2 mM) do not allow achieving complete degradation of mononitrophenols. Some examples of incomplete degradation of nitrophenols are presented in Fig. 3. As can be seen, the degradation rate is high enough at the initial stage of the process, but later the reaction is retarded and then restrained so that no further degradation takes place. The residual concentration of hydrogen peroxide measured immediately after the treatment was zero in these cases. Hydrogen peroxide seems to be the limiting compound as even application of relatively high concentrations of the catalyst (1 mM) also leads to incomplete degradation of the target compound.

A comparison of the degradation rates of different nitrophenols revealed (Fig. 4) that mononitrophenols are degraded more easily than dinitrophenols, and dinitromethylphenols are relatively the most stable. According to the 90% conversion time of nitrophenols given in Table 2 and Fig. 4 the order of the destruction of nitrophenols is as follows:

2-NP > 4-NP > 2,5-DNP > 2,6-DNP > 4,6-DN-*o*-CR ≥ 2,6-DN-*p*-CR.

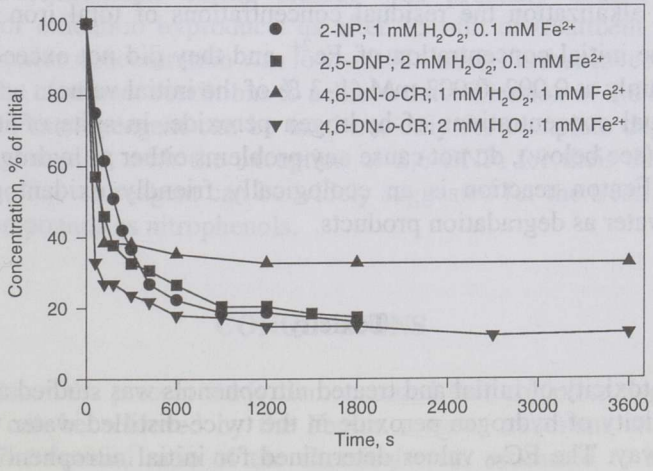

Fig. 3. Incomplete degradation of 4,6-DN-*o*-CR, 2-NP, and 2,5-DNP.

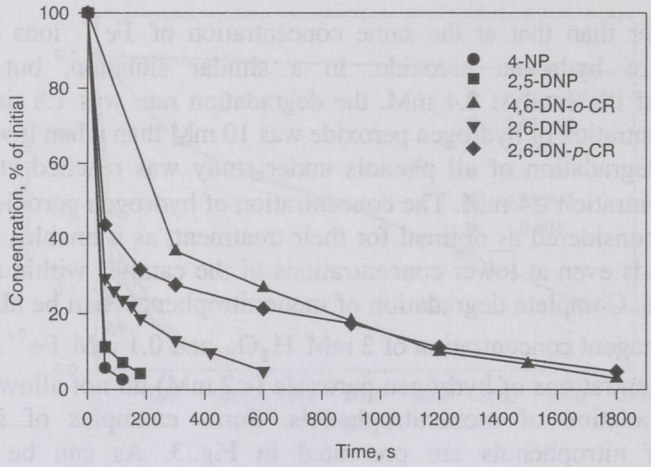

Fig. 4. Degradation of various nitrophenols during the Fenton reaction with the concentration of hydrogen peroxide 4 mM and Fe^{2+} 0.4 mM.

The results of the present investigation demonstrated that under suitable conditions complete degradation of all phenols studied can be achieved. Nitrophenols can be successfully degraded by the Fenton reagent treatment with the optimal ratio of chemicals being hydrogen peroxide:phenol 10:1 and catalyst (Fe^{2+}): phenol from 1:1 to 1:2.

The residual iron should not cause any environmental problems as it can be removed by alkalization of the solution. Iron is precipitated at pH≥9.0 in the form of $Fe(OH)_3$ [19]. Therefore, the residual concentration of total iron in the samples was measured after the alkalization of the Fenton reagent treated sample. Indeed, after alkalization the residual concentrations of total iron were much lower than the initial concentration of Fe^{2+} and they did not exceed 0.05 mM, remaining mainly at 0.002–0.003 mM (1–3 % of the initial value).

The residual concentrations of hydrogen peroxide, in spite of its relatively high toxicity (see below), do not cause any problems either as hydrogen peroxide used in the Fenton reaction is an ecologically friendly oxidant giving only oxygen and water as degradation products.

Toxicity

The acute toxicity of initial and treated nitrophenols was studied according to [16]. The toxicity of hydrogen peroxide in the twice-distilled water was studied in the same way. The EC_{50} values determined for initial nitrophenols and their toxic effects after treatment are listed in Table 3. The mortality of *D. magna* in control tubes was 0% in all tests. Among the compounds studied 4,6-DN-*o*-CR

Table 3. EC_{50} values for initial nitrophenols and the toxic effects after treatment (4 mM of H_2O_2 added)

Compound	EC_{50} values for initial nitrophenols, mg/L	Conditions of treatment		Toxic effects after treatment
		Fe^{2+} added, mM	Duration, min	
4,6-DN-*o*-CR	4.62±0.41	1	15	Not toxic after 2 days from the treatment; EC_{50} = 20.5% immediately after the treatment
2,6-DN-*p*-CR	29.0±3.3	0.85	20	Not toxic
2,5-DNP	21.9±2.0	0.1	45	Not toxic
2,6-DNP	38.0±2.5	0.1	60	Toxic, EC_{50} = 57.6%
4-NP	28.2±1.5	1	30	Not toxic
		0.1	15	Not toxic
2-NP	218±11	0.1	20*	Not toxic

* 2 mM of H_2O_2 added.

was the most toxic. All other phenols, except 2-NP, were also quite toxic. High toxicity towards *D. magna* was determined also for hydrogen peroxide, for which EC_{50} was 0.121±0.020 mM or 4.11±0.68 mg/L. However, as it is easily degraded by light hydrogen peroxide is not potentially dangerous when the treated influent is discharged into water bodies.

The treated samples, except 2,6-DNP, are not toxic (see Table 3). For 4,6-DN-*o*-CR the changes in toxicity were evaluated immediately after the treatment and two days later. Immediately after treatment the solution was still toxic, but its toxicity was lower than of the initial solution. The EC_{50} values were 20.5% and 5.8%, respectively. Two days later the solution of 4,6-DN-*o*-CR was not toxic. Detoxification during storage was probably caused by further degradation of oxidation byproducts as after 15 min of treatment the residual hydrogen peroxide concentration was low – 0.014 mM. Further investigations are required on the treatment conditions to achieve detoxification of 2,6-DNP.

Thus, the Fenton reagent can be used not only for complete degradation of nitrophenols, but also, with the exception of 2,6-DNP, for their detoxification. Therefore, the Fenton reagent can be widely suggested for the treatment of such hazardous compounds as nitrophenols.

CONCLUSIONS

The results of the present study demonstrated that complete degradation of nitrophenols can be achieved by the Fenton reagent treatment under suitable conditions. The optimal ratio of the chemicals was estimated to be hydrogen peroxide:phenol 10:1 and catalyst (Fe^{2+}):phenol from 1:1 to 1:2.

As hydrogen peroxide concomitantly used in the Fenton reaction is an ecologically friendly oxidant whose only degradation products are oxygen and water, its residual concentrations do not cause any problems. The residual iron can be removed by alkalization of the solution and subsequent precipitation and thus it does not cause any environmental problems either.

Thus, as the Fenton reagent can be used not only for complete degradation of nitrophenols, but also, with the exception of 2,6-DNP, for their detoxification it can be widely suggested for the treatment of wastes containing them.

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NITROFENOOLIDE LAGUNDAMINE FENTONI REAKTIIVIGA

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Töö eesmärk oli uurida mõnede nitrofenoolide (2-nitrofenool, 4-nitrofenool, 2,5-dinitrofenool, 2,6-dinitrofenool, 4,6-dinitro-2-metüülfenool, 2,6-dinitro-4-metüülfenool) lagunemist ning detoksifitseerimist kasutades Fentoni reaktiivi. Selgub, et nitrofenoolid lagunevad Fentoni reaktiivi toimel kiiresti, kui nitrofenooli ja vesinikperoksiidi omavaheline vahekord on 10:1 ning katalüsaatori (Fe^{2+}) ja nitrofenooli vahekord on alates 1:1 kuni 1:2. Reaktsiooni kiirus sõltub vesinikperoksiidi ja katalüsaatori (Fe^{2+}) kontsentratsioonist. Raua jääke on võimalik eraldada sadestamise ja filtreerimise teel. *Daphnia magna* test, mis on levinuim akuutse toksilisuse määramiseks vesikeskkonnas, näitab, et nitrofenoolide töötlemine Fentoni reaktiiviga viib nende täieliku detoksifitseerimiseni (välja arvatud 2,6-dinitrofenool).