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Frantisek Kastanek[a]; Ywette Maleterova[a]; Petr Kastanek[b]
[a] Institute of Chemical Process Fundamentals, Academy of Science of the Czech Republic, Czech Republic [b] Prague Institute of Chemical Technology, Technická

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Combination of Advanced Oxidation and/or Reductive Dehalogenation and Biodegradation for the Decontamination of Waters Contaminated with Chlorinated Organic Compounds

Frantisek Kastanek and Ywette Maleterova
Institute of Chemical Process Fundamentals, Academy of Science of the
Czech Republic, Rozvojova Czech Republic

Petr Kastanek
Prague Institute of Chemical Technology, Technická

Abstract: The method of decomposition of chlorinated organic substances in contaminated water based upon successive steps of chemical pretreatment of organic compound with a) active radicals (Fenton reaction) and/or with b) reductive dehalogenation on metallic Pd in the presence of zero-valent iron, followed by aerobic biodegradation using bacteria strain *Pandoraea sp*. was studied. 4-chlorophenol was chosen as a model compound. Generally, chlorophenols show limited biodegradability. The average efficiency of biodegradability of 4-chlorophenol with both free and immobilized cells does not exceed 70% after 42 days of biodegradation, but their intermediates obtained by partial oxidation (products of hydrolytic-hydroxylation) and/or a product of their partial reductive dechlorination (phenol) show increased biodegradability. To test the efficiency of the method, water exposed to this contaminant was treated in the laboratory in batch conditions. Because the products of partial oxidation and partial reductive dehalogenation of 4-chlorophenol essentially differ, the main factor studied was the efficiency of biodegradation of 4-chlorophenol after oxidative or reductive pre-treatment steps. In comparison with the rate of biodegradation using free cells without application of the pre-treatment step, the rate of degradation of 4-chlorophenol by the application of consecutive combination of Fenton reagent and

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Address correspondence to Frantisek Kastanek, Institute of Chemical Process Fundamentals, Academy of Science of the Czech Republic, 165 00 Prague 6, Rozvojova 135, Czech Republic E-mail: kastanek@icpf.cas.cz

biotreatment was two-fold. As for the combination of reductive dechlorination pre-treatment step with consecutive biodegradation, the rate of decontamination of the 4-chlorophenol was a little bit higher here in comparison with the rate of biotreatment after the pre-oxidizing step: the remaining concentration of 4-chlorophenol corresponding to the sampling in 7, 28, and 56 days after the inoculation were 70 mg/L, 12 mg/L, and 1.1 mg/L, respectively, in samples containing the average initial concentration of 126 mg/L of 4-chlorophenol. Positive results may probably be due to the co-substrate effect of phenol presented in the samples after the pretraetment reductive step. We have shown that both procedures followed with aerobic biodegradation can be considered suitable for removing hazardous chlorinated compounds from contaminated waters. The rate of biodegradation after the application of pre-treatment procedures was slightly enhanced in comparison with the rate of biodegradation without the application of the pre-treatment steps. It is evident that the choice of the decontamination pre-treatment procedure cannot be generalized and will essentially depend upon the type and concentration of target contaminants and on process costs.

Keywords: Advanced oxidation, Fenton reaction, reductive dehalogenation, zero-valent Pd/Fe, consecutive aerobic biodegradation, 4-chlorophenol

1 INTRODUCTION

Advanced oxidation processes (AOP) are particularly appropriate for effluents containing refractory, toxic, or non-biodegradable materials. The purpose of all AOPs is to produce active hydroxyl radicals (*OH), a highly reactive oxidizing agent that reacts with and destroys most of the organic pollutants in water and soils (1–9). However, the use of AOP may be limited because costs may be higher than competing technologies due to energy requirements and higher capital costs (UV) and reagents costs (H_2O_2).Results showed that processes producing *OH radicals without the need of UV- irradiation proved also to be suitable for the oxidation of many organic components in waste waters. A potential viable solution proposed during the last two decades with the aim of improving the economy and to obtaining optimal decontamination results is a combination of AOP and biological processing (10–16). The biodegradability enhancement was observed as a result of AOP treatment thus allowing the recommendation of AOP as a pre-treatment procedure for waste water purification. It was found that combined chemical and biological treatment was more effective than either one alone and can be used as a successful technology for industrial waste water remediation. The pre-treatment of waste water through AOP leads in some cases to less toxic and more degradable intermediates thus ensuring the stability and efficiency of the following biological treatment step. Regardless of the individual pollutant species, the Fenton reagent proves to be a very powerful oxidizing agent. There are, however, chlorinated species which are resistant to oxidation by Fenton reaction and each case should be independently analyzed (17).

Comparing the coupled abiotic-biotic process with biological treatment, the applied pre-oxidation step also did not always lead to a significant improvement in biodegradation (7).

At present, one of the most challenging environmental tasks is the decontamination of soils and underground water contaminated by aromatic halogenated compounds. Under certain circumstances, retardation in biodegradation and/or an increase in toxicity may also be observed within the AOP treatment step. In the last few years, there has been great interest in assessing the use of reducing metals for the treatment of chlorinated compounds, where the possibility of production of toxic intermediates during the treatment was hindered. Many laboratory and industrial tests have shown that scrap iron particles produce rapidly ending extensive reductive dechlorination of many organic chlorinated compounds. Our preliminary investigation, however, clearly demonstrated that iron particles by themselves cannot attack chlorinated aromatic compounds. We have recently shown (18) that only a bimetallic system (Pd catalyst deposited on different supports in the presence of zero-valent Fe, e.g.) can be considered suitable for the treatment of water contaminated by aromatic chlorinated and poly-chlorinated compounds. Biological treatment (both aerobic and anaerobic) is often limited by the presence of recalcitrant organics, like the above-mentioned aromatic chlorinated compounds. Fenton oxidation and/or reductive dehalogenation may be used as a pre-treatment procedure for preliminary abatement of the chlorine load and to favor biological oxidation.

4-chlorofenol shows reduced biodegradability (19), but intermediates of partial oxidation (4-chloro-p-benzoquinone) and/or the product of reductive dehalogenation (phenol) are supposed to show increasing biodegradability. In these combined processes, the chemical process would be utilized as a pre-treatment step with the aim of modifying the chemical structure of the pollutant in order to transfer it into biodegradable intermediates, and so enhance the biodegradability. The point in which it is suitable to stop the Fenton reaction and/or reductive dechlorination and to start the biological process is the subject of this investigation as well.

MATERIALS AND METHODS

Preparation of Pd/Fe Catalyst

Palladized steel wool (obtained from LUX-Werkzeuge, Wemelskirchen, Germany, extra-fine 00, the average diameter of the steel fibers was roughly 26 micrometers) was prepared by the reaction of K_2PdCl_4 with Fe-fibers (18). The average concentration of Pd in the steel wool was 0.05 wt.%.

Biodegradation of 4-Chlorophenol, Mineral Medium, and Procedure

Free Cells

The mineral medium is a mixture of 10 ml of solution A (7 g K_2HPO_4, 3 g KH_2PO_4, 1 g NaCl in 200 ml of H_2O) + 0.1 ml of solution B (4.2 g Na_2SO_4 in 30 ml of H_2O) + 0.1 mL of solution C (4.5 g $MgCl_2 \cdot 6H_2O$ in 30 ml H_2O + distilled to form 100 ml of mineral medium.

The dosages of pure 4-chlorophenol (301–313 mg/L) were added to 100 mL of the mineral medium in an Erlenmayer flask jointly with 10 mL of inocula of the preliminary selected bacterial strain *Pandoraea sp.* UH 222 and UH 2222 (obtained from the collection of the Institute of Microbiology and Biochemistry, Prague Institute of Technology. The average density of cells in inocula was 10^{13}/mL) Strains that were taxonomically identified by A6S rDNA as *Pandoraea* were able to use some chlorobenzoic acids and PCBs as sole carbon sources (20) and we have trained these strains to also give the cells the ability to utilize chlorophenols as well. The average original concentration of 4-chlorophenol in the solution was between 301 mg/L and 313 mg/L. The flasks were capped and placed in a wrist-action shaker. The course of the biological decomposition was followed by periodically withdrawing a 1-microL sample of the solution. The analysis of blanks and samples kept in the dark established that only biological exposure caused degradation. Reproducibility was investigated by running the samples in triplicates. In typical experimental conditions the samples were analyzed after 0, 7, 14, 21, and 42 days of inoculation.

Immobilized Bacteria

The strains of *Pandoraea sp.* UH 2222 (samples No. 1 and 2) and UH 222 (samples No. 3 and 4) were immobilized in polyurethane foam cubes (10 mm) by physical adsorption (being 48 hours in the contact with porous foam in mineral medium) and the biocatalyst was then inserted in Erlenmayer flasks containing mineral media and 4-chlorophenol. The rate of the volume of the catalyst and aqueous medium was 1:3, the density of cells in the biocatalyst was estimated from the balance of the density of cells and mass of liquid absorbed in foam in the course of adsorption of microorganisms as approx. $3 \cdot 10^{12}$ cells in cm^3.

Chemicals Used

The chemical were obtained mainly from Aldrich.

Chemical purity was: palladium (II) chloride, 99.9+%, K_2PdCl_4, 99%, 4-chlorophenol, 99+%, H_2O_2 (36% solution in water, A.C.S. reagent, LACHEMA, Czech Republic), iron (II) sulfate heptahydrate 99+%.

Analytical Procedure

Samples of chlorinated phenol were acidified by H_3PO_4 and after adding Na_2SO_4, 4-chlorophenol was extracted in ethyl acetate. After the acetylation of such a solution with acetanhydride/pyridine, the obtained product was analyzed by GC-MS (GC: HP 6890, MS: HP 5973) as acetyl derivate.

Fenton Reaction

To test the efficiency of the AOP (Fenton reagent), 200 mL of water in 500 mL Erlenmayer flasks was spiked with the contaminant (approx. 1.5 g of 4-chlorophenol) and with various amount of reagents (approx. 0.1, 0.2, 2.8 and 14 g of $FeSO_4 \cdot 7H_2O$) at pH 3. Instead of the sulphate Fe(II), solid steel wool was added to the flask as a catalyst in one experiment. The solution of H_2O_2 in water (36%) was periodically added to the reaction solution in the aliquots of 1 mL in time interval of 10 minutes. The total amount of peroxide added during 170 minutes of the experiment was 17 mL. The course of the temperature during the experiments was also measured. The reaction temperatures surprisingly increased in the course of the experiments to the values of approx. 40°C, perhaps due to the very high initial concentration of reaction compound.

Reductive Dehalogenation

In typical experimental conditions, the initial concentration of 4-chlorophenol varied between 300 mg/L and 400 mg/L, while the mass ratio of the catalyst (0.05 wt.% of Pd) to contaminated water was 0.014 : 1. The flasks were kept at 25°C in the dark to prevent photo-decomposition of 4-chlorophenol.

Combination of Fenton Reaction and Biotreatment

200 ml of water was added to individual Erlenmayer flasks together with Fe(II) sulfate heptahydrate, or pure steel wool, or palladized steel wool. The samples were spiked with 4-chlorophenol (approx. 1.5 g), the acidity was adjusted to pH 3, see Table 1. To the individual samples 1 mL of 36% H_2O_2 in time intervals of 10 minutes was periodically added (4 mL, 5 mL, and 10 mL of the aqueous solution of hydrogen peroxide was added to the samples in the total). After the reaction was stopped, the remaining concentration of 4-PC was determined. Consequently, the acidity of the solution in the individual samples was adjusted to pH 6.5 and the samples were inoculated by the strain *Pandoraea sp*. UH 2222. In general, 10 volume% of the liquid inocula containing 10^{13} cells/mL was inoculated in the reaction volume in the flask, without adding any other nutrients (the 4-chlorphenol was

Table 1. Reaction conditions, 200 ml of the distilled water

Sample	Catalyst	Inlet concentration of 4-PC, g
FI/1	2.8300 g $FeSO_4 \cdot 7H_2O$	1.5033
FI/2	0.2834 g $FeSO_4 \cdot 7H_2O$	1.5017
FI/3	1.1590 g Fe-wool (pure)	1.5018
FI/4	1.2249 g Pd/Fe wool (0.05% Pd)	1.5077

supposed as the only source of carbon for microorganisms). The flasks were capped and placed in a wrist-action shaker. The samples were shaken at intensity 2 s^{-1}. The course of the reaction was followed by periodically withdrawing a 1-microL sample of the solution. The temperature was maintained at 25°C, and the samples were kept in the dark. The course of the reaction was monitored by the continuous measurement of the red-ox potential.

RESULTS

Biodegradation of 4-Chlorophenol-Biodegradation with Free and Immobilized Cells

The results (by running the samples in triplicates) are summarized in Table 2 and Table 3.

In comparison with the efficiency of the biodegradation of free and immobilized cells we can conclude, that the highest efficiency of biodegradation obtained (almost 80%) was achieved with immobilized cells (the strain *Pandoarea sp*. UH 2222), however, the total decomposition of 4-chlorophenol was by far not completed within the term of 30 days.

The course of the depletion of 4-chlorophenol by biodegradation can be approximately described by the kinetic of 1st order. The estimations of reaction rate constants for free cells were $k_{\mathrm{UH}\ 222} = 0.021\ \pm 0.002$ day^{-1} and $k_{\mathrm{UH}\ 2222} = 0.029 \pm 0.005$ day^{-1}, respectively.

Table 2. The concentration of 4-chlorophenol (in mg/L) in the course of biodegradation with free cells of *Pandoraea sp*

Strain/days of biodegradation	0	7	14	21	42
UH 222	313	264	238	212	131
UH 2222	302	232	202	191	90

Average values are mentioned running the samples in triplicates, the maximum deviations were ±28% in the experimental data obtained after 42 days.

Table 3. The concentrations of 4-chlorophenol (in mg/L) in the course of biodegradation with immobilized cells of *Pandoraea sp*

Sample	Mass of the carrier, g	Concentration of 4-chlorophenol			
		Initial	After 10 days	After 20 days	After 30 days
1	0.386	308	139	81	64
2	0.387	305	143	85	71
3	0.381	369	262	162	136
4	0.388	327	219	129	125

Average values are mentioned running the experiments in triplicates. Maximum deviation of the data was ±26% after 30 days.

Efficiency of Fenton Method of Degradation of 4-Chlorophenol (4-CP) (After 170 minutes of the Reaction Time)

The results (by running the samples in triplicates) are summarized in Table 4.

The destruction of 4-CP was almost total at the reaction conditions applied (consuming finally 17 mL of 36% H_2O_2). The concentration of the catalyst achieved the optimum value when the mass ratio of Fe(II) to 4-CP was 0.38:1 (or 0.57 g Fe(II) to 1.5 g of 4-CP), the ratio of H_2O_2 (pure) to Fe(II) was 6.12 mL to 0.57 g (or 10.7 mL of H_2O_2 and 1 g of Fe(II)), or approx. 37 mole H_2O_2/mole 4-CP. These findings are in concordance with previously published data (see 21, 22). Although the efficiency of decontamination of 4-chlorophenol by the application of active hydroxyl radicals is very high, the consumption of the expensive reagent is also remarkable. Therefore, the effort to apply the combination of the Fenton reagent and biotreatment with the aim of economizing the consumption of the reagent seems justifiable.

Table 4. The efficiency of AOP degradation (Fenton) of 4-chlorophenol

$FeSO_4 \cdot 7\ H_2O$, g	Initial conc. of 4-CP, g	Temperature (max),°C	Final conc. of 4-CP, mg/L[b]
0.142	1.515	35.4	0.34(±0.26)
0.283	1.501	41.3	0.18(±0.14)
2.830	1.500	45.5	0.04(±0.03)
14.264	1.503	40.7	0.72(±0.51)
1.403[a]	1.504	40.9	0.03(±0.03)

[a] Pure steel wool (non palladized).

[b] According to the recommendation of the Czech Ministry of Environment, the allowable limit of the pollution of underground water with sole chlorinated phenol is 0.01 mg/L.

Degradation of 4-Chlorophenol with Palladized Steel Wool

During the 360 minutes of contact the efficiency of dehalogenation reached approximately 35% and did not increase with further treatment. The conversion of 4-chlorophenol was low, but some positive influence of the Pd/Fe catalyst on reductive dechlorination was evident as the phenol was confirmed as a product. Certain resistance of this isomer to rapid dechlorination has also been demonstrated in the other paper (21). However, the occurrence of biodegradable phenol in the course of the reductive dechlorination is favorable for a combination of chemical pre-treatment and consecutive biotreatment (23).

The average concentration of phenol obtained in these experiments (obtained from 3 independent measurements) surprisingly did not fit the theoretical mass balance, and the difference was substantial (the average amount of phenol detected was 39 mg/L ±4 mg/L). More work is needed to determine the reaction mechanism and reaction pathways of reductive dechlorination of this specie (and, generally, of chlorination aromatic compounds).

Combination of Fenton Reagent and Biotreatment

The results are summarized in Table 5.

The total amounts of hydrogen peroxide of 4 and 5 or 10 mL (added as Fenton reagent) was no doubt sufficient to substantially abate the concentration of 4-PC already in the primary step of chemical oxidation, nevertheless, the application of another decontamination procedure would be necessary in order to comply with the demanded clear-up limit (which is theoretically <0.01 mg/L of 4-chlorophenol tolerated in underground water).

The average value of the reaction rate constant corresponding to these experiments has been estimated as $k_{\mathrm{av,UH2222}} = 0.059 \pm 0.016\,\mathrm{day}^{-1}$ (for concentrations of 4-CP >25 mg/L).

In general, most authors tend to correlate the kinetic data with the formal kinetics of the 1st order. However, by calculating the rate constants they seem to be not independent from concentration of 4-chlorophenol and the values calculated by first order kinetics are obviously comparable only in solutions with similar 4-chlorophenol concentration (21).

In spite of the absence of supporting nutrients and minerals in biologically treated solutions and having in mind possible divergences of experimental data obtained in the course of the complicated combined decontamination processes, we can with some caution conclude that partial oxidation enhances biodegradability of toxic 4-chlorophenol. In comparison with the rate of biodegradation using free cells without application of the pretreatment step (see section 3.1) the rate of biodegradation here was twofold. Considering that for almost total depletion of the organic compound

Table 5. The results of biodegradation of 4-CP with free cells of *Pandoraea sp*. UH 2222 after the pre-treatment with the Fenton reagent

		4-PC after biodegradation, in days		
Sample	4-PC after the pre-treatment	7	14	21
10 mL of H_2O_2 (36%) was added				
FI/1	84 (±9)	49 (±5)	22 (±4)	14 (±4)
FI/2	125 (±14)	97 (±11)	55 (±6)	38 (±6)
FI/3	12 (±4)	1.6 (±1)	0.2 (±0.1)	0.02[a] (0.04)
FI/4	25 (±4)	2.3 (±0.8)	0.4 (±0.25)	0.051[a] (1.02)
5 mL of H_2O_2 (36%) was added				
FI/1	475 (±61)	334 (±53)	201 (±14)	132 (±15)
FI/2	382 (±64)	246 (±18)	119 (±35)	88 (±29)
4 mL of H_2O_2 (36%) was added				
FI/1	677 (±98)	383 (±99)	373 (±96)	296 (±90)

[a] Average from 3 measurements, the concentration of 4-chloropenol in one experiment was non-detected.

The amount of hydrogen peroxide added during the course of the reaction was of 4 and 5 or 10 mL of H_2O_2 (36%) respectively. Average values of the 4-chlorophenol (from 3 measurements) were written down. In parenthesis maximum deviation in mg/L experimentally obtained there are reported. The concentrations of 4-PC are in mg/L. The indication of samples corresponds to Table 1. Initial concentration of 4-PC was approx. 1.5 g in 200 mL.

Table 6. The course of biodegradation of aqueous solution of 4-chlorophenol with free cells of *Pandoraea sp.* after the pre-treatment step of partial reductive catalytic dechlorination with Pd/Fe catalyst

	Concentrations of 4-chlorophenol (mg/L)					
	Pre-treatment step		Biodegradation, in days			
Time	0	6 hours	0	7	28	56
Concentrations	360	124 (±12)	124	70 (±17)	12 (±2.4)	1.1 (±0.4)

Initial concentration of 4-chlorophenol was 360 mg/L, after the pre-treatment step 20 mL of inocula solution containing approx. 10^{13}cells/mL to 200 mL of the solution was added. The temperature was kept on 25°C, pH during biodegradation was maintained constant pH 6.5.

from the solution, huge amounts of the oxidant is required, biological treatment of pre-treated waste waters, which is undoubtedly cheaper, appears as a reasonable decontamination alternative also for some chlorinated organics. It is evident that the choice of the decontamination method cannot be generalized and will depend on the type of contaminants, real conditions (biodegradation is very time consuming), and process costs.

The choice of the proper time-instant when the pre-treatment step should be stopped can be unambiguously determined as a compromise among many factors in consideration, such as operation time required for the decontamination, the volume of the contaminated water, and the concentration of target compounds, operational and investment costs, etc.

Oxidation-reduction potential (ORP) monitoring is a useful method for determining the decomposition efficiency of the target compound and to determine the proper time for a change of procedures. There is a slight increase in the ORP with increasing Fe(II) dosages, and an apparent increase with increasing the addition of hydrogen peroxide was observed. In the course of the reaction a perceptible decrease of the ORP is evident. The periodical dosage of H_2O_2 can be easily controlled by monitoring the time changes of ORP, see Fig. 1.

The Combination of Reductive Dechlorination Pre-treatment with Consecutive Biodegradation

The procedure was similar to the one applied in the oxidizing pre-treatment. In samples (200 mL aqueous solution containing at average 126 mg/L of 4-chlorophenol) remaining after the partial reductive dehalogenation (see paragraph 3.3) the level of acidity was adjusted to the value of pH 6.5 and the liquid content in the flasks was inoculated with inocula of free cells of *Pandoraea sp.* UH 2222 (20 mL of the inocula solution,

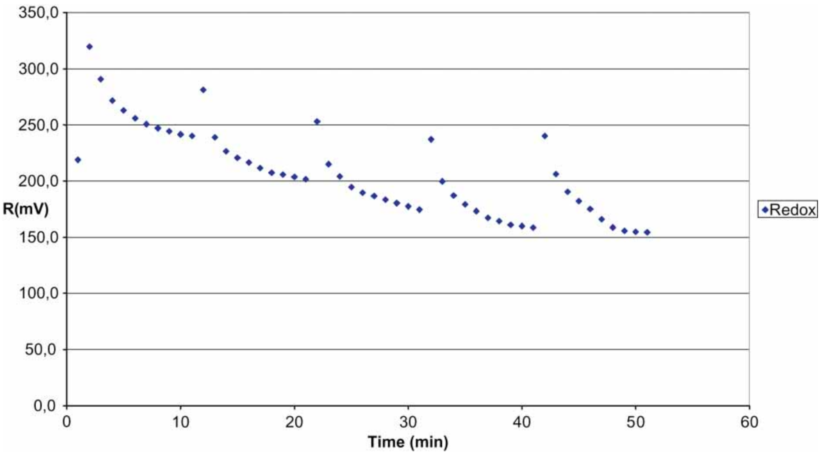

Figure 1. The course of the red-ox potential (mV) during the pre-treatment step (the total amount of aqueous solution of H_2O_2 added was 5 ml, see Table 5).
The peak values of re-dox potential correspond and indicate the periodically added aliquots of peroxide to the reacting system followed by consecutive time-damping of re-dox potential values when peroxide is consumed by Fenton reaction.

containing approx. 10^{13} cells/ml was added). The temperature was maintained at 25°C, the flasks were kept in the dark, and placed in a wrist-action shaker. The rate of decontamination of the 4-chlorophenol was a little bit higher here, $k_{\mathrm{av,UH2222}} = 0.0065 \pm 0.018\ \mathrm{day}^{-1}$, in comparison with the rate of biotreatment after the pre-oxidizing step (it is, however, questionable, if this difference in values of kinetic constants is relevant, keeping in view the deviations of experimental data): the remaining concentration of 4-CP corresponding to the sampling in 7, 28, and 56 days after the inoculation were 70 mg/L, 12 mg/L, and 1.1 mg/L, respectively. The average values of maximum deviation were ±27%, the maximum value of deviation was obtained in the experiment after 56 days (positive deviation +36% in one experiment were detected). Slightly positive results may probably also be due to the co-substrate effect of phenol presented in the environment at the beginning of the biodegradation. In the case of the advanced oxidation procedure the scarcely presented amounts of peroxide perhaps remaining after the pre-treatment step was not destroyed in samples submitted to following biodegradation: we have controlled the presence of peroxide only indirectly by monitoring the oxidation-reduction potential, see Fig. 1. However, some potentially presented traces of H_2O_2, if any, could somewhat influence the biological activity and the slight decrease of the rate of biodegradation in comparison with reductive pre-treatment could be explained with this phenomena. Further study and optimization of both of these methods of decontamination are urgently needed.

CONCLUSION

The consecutive decomposition of 4-chlorophenol in aqueous solutions by active radicals (Fenton reaction) and/or by reductive dehalogenation on bimetallic Pd/Fe catalyst followed by aerobic biodegradation by the selected bacteria *Pandoarea sp.* was studied. To test the efficiency of both the pre-treatment methods, water exposed to this contaminant in the laboratory was treated in batch conditions. We have shown that partial oxidation and/or reductive dechlorination of 4-chlorophenol enhances biodegradability, though the products of the oxidative and reductive partial chemical decomposition were different. In both cases the chemical pre-treatment somewhat enhanced the successive step of biodegradation. The chemical pre-treatment seems to be a feasible method for acceleration of biodegradation of organics, namely chlorinated aromatic compounds. The combined application of the Fenton reagent and biotreatment can economize the material costs of oxidative pre-treatment. The pre-treatment mode of reductive dechlorination in comparison with Fenton oxidation is less costly as regards to the investment and operating costs; however, the weak point of the reductive method is a tendency to gradual blocking of the catalyst surface by inorganic precipitates when treating waters originating from polluted industrial sites. Therefore, the reductive method can be preferentially applied for less contaminated wastewater. It is evident that the choice of the method cannot be generalized and will depend upon the type of contaminants, real conditions a process costs. Further study and optimization of both of these methods of decontamination of halogenated compounds in aqueous solutions is urgently needed.

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