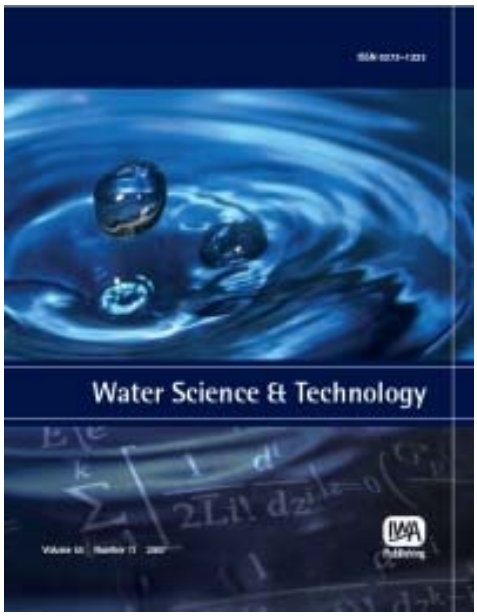

Combination of hydrodechlorination and biodegradation for the abatement of chlorophenols

Shiwei Zhou, Xin Jin, Feifei Sun, Hao Zhou, Cuiyun Yang and Chuanhai Xia

ABSTRACT

A method for abatement for chlorophenols (CPs) in contaminated water based on successive steps of catalytic hydrodechlorination (HDC) over Pd/C at ambient temperature and pressure, followed by aerobic biodegradation using yeast *Candida tropicalis* (*C. tropicalis*) was studied. The results showed that 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) could be easily and completely dechlorinated under mild conditions, ultimately yielding phenol as product. Subsequently, phenol (0–900 mg L^{-1}) could be completely degraded by *C. tropicalis* within 30 h. Moreover, during the biodegradation of phenol, definite mass of ethanol ($\leq$0.5%) caused a modest increase in the duration of the lag phase, but led to a great increase in the maximum degradation rates. This means that CPs with higher concentration could be efficiently detoxified under mild conditions by a combination of HDC and biodegradation in water or water–ethanol systems.

Key words | biodegradation, *Candida tropicalis* (*C. tropicalis*), chlorophenol (CP), ethanol effect, hydrodechlorination (HDC)

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INTRODUCTION

Chlorophenols (CPs) are present in wastewaters of paper and pulp, pesticides, dyes, textiles, pharmaceuticals, and petrochemicals. Most of them have been listed as priority pollutants due to their high toxicity and hard biodegradability. Thus, safely disposing of these compounds is becoming an important area of research with the increasing concern about the environment.

Various abatement techniques, including biological, thermal and chemical treatments have been developed in the last few years for the detoxification of organic pollutants (Laine & Cheng 2007; Busca *et al*. 2008). Biological treatments usually require a long residence time for microorganisms to degrade the pollutant, because they are affected by CP toxicity; thermal treatments present considerable emission of other hazardous compounds; and chemical treatments, which include processes such as flocculation, precipitation, adsorption, oxidation and reduction, require a post-treatment to remove the pollutant or secondary pollutant (Pera-Titus *et al*. 2004). In fact, the complete removal of organic halides such as CPs from water is very difficult by a single technique due to the high cost or limitation. So, hybrid methods become imperative for the abatement of organic halides (Gogate & Pandit 2004).

Most of the hybrid methods focus on the combination of advanced oxidation processes (AOPs) and biological degradation (Essam *et al*. 2007; El-Gohary *et al*. 2009; Molina *et al*. 2010; Oller *et al*. 2011). Only Ghoreishi & Haghighi (2003) investigated the decolorization of textile dyeing wastewater by a combined reduction-biological treatment system. Polychlorinated phenols have higher thermostability and stronger nonbiodegradability owing to the presence of chlorine in the aromatic ring. For example, in our previous study (Zhou *et al*. 2011), the needed time was more than 9 h for catalytic peroxide oxidation of 2,4,6-trichlorophenol (2,4,6-TCP) over Cu–Al hydrotalcite/clay composite at 40 °C. However, the times were only 40 and 13 min for the oxidation of 4-chlorophenol (4-CP) and phenol, respectively, under the same experimental conditions. This means that disposing effectively of polychlorinated phenols by combination of chemical oxidation and biological treatment is also difficult.

We believed that dechlorination was the key and precondition for the abatement of CPs. A number of workers have studied the dechlorination of organic halides, and catalytic hydrodechlorination (HDC) was considered as one of the most promising and innovative techniques, because it

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could convert the toxic organic chlorides into the corresponding hydrocarbons under mild conditions (Menini *et al.* 2000; Ukisu *et al.* 2000). Thus, combination of HDC and biodegradation for abatement of CPs is interesting and promising. However, the combination method has not been reported. Furthermore, the effect of ethanol on microbial degradation of phenol is a prior consideration during the combination of HDC and biodegradation for abatement of CPs, because the HDC of organic halides is usually performed in ethanol–water systems in view of their dissolvability (Wee & Cunningham 2008; Gómez-Quero *et al.* 2010).

In this work, we, therefore, studied the combined method of HDC and biodegradation for abatement of 4-CP and 2,4-dichlorophenol (2,4-DCP). Additionally, the effect of ethanol on microbial degradation of phenol was also investigated. The aim is to develop a simple, mild and efficient method for the abatement of non-biodegradable organic wastewater pollutants.

MATERIALS AND METHODS

Pd/C catalyst

Five per cent Pd/C catalyst supplied by C&P Chemical Co., China was hermetically sealed and kept in a desiccators before the experiments. Its physical properties were characterized as follows: particle diameter (60 μm), BET surface area (1,100 $m^2 g^{-1}$), pore volume (0.66 $cm^3 g^{-1}$), and average pore diameter (2.3 nm).

Microbial strain

According to the method of Jiang *et al.* (2005), a highly effective degradation strain of phenol was isolated from the sludge collected from one of the sewage pipes buried in the beach of Yellow Sea in Yantai, China. Based on physiological and biochemical tests and 26S rDNA sequence analysis by Takara Biotechnology (Dalian, China) Co., Ltd, it was identified as *Candida tropicalis* (*C. tropicalis*), due to it being 100% homologous to *C. tropicalis* NT22 (GenBank accession no. AB557860.1) and *C. tropicalis* PA-M13 (GenBank accession no. GU373782.1).

Degradation of phenol by *C. tropicalis*

Growth of *C. tropicalis* and the biodegradation of phenol were carried out at 30 °C in 100 mL shaking flasks on a rotary shaker (200 rpm). The flasks contained 25 mL mineral salts medium (MSM) with 300–900 mg L^{-1} of phenol and 10^6 cells mL^{-1} of *C. tropicalis*. The MSM contained NH_4NO_3 (1.0 g L^{-1}), KH_2PO_4 (0.5 g L^{-1}), $K_2HPO_4{\cdot}3H_2O$ (0.5 g L^{-1}), $MgSO_4{\cdot}7H_2O$ (0.2 g L^{-1}), NaCl (0.2 g L^{-1}), $CaCl_2$ (0.1 g L^{-1}), $MnSO_4{\cdot}H_2O$ (10 mg L^{-1}), and $FeCl_2$ (10 mg L^{-1}).

Under each condition, sterile medium was used as the control to evaluate the degree of phenol removal due to volatilization or photodegradation. All experiments were repeated three times, and the data shown were the mean values.

Further, the effect of ethanol on biodegradation of phenol was also performed at 30 °C in 100 mL shaking flasks on a rotary shaker (200 rpm). The flasks contained MSM (25 mL), phenol (800 mg L^{-1}), ethanol (0–0.80%), and *C. tropicalis* (0.5×10^6 cells mL^{-1}).

Catalytic HDC of CPs over Pd/C

According to the method in our previous study (Xia *et al.* 2009), the HDC reaction was carried out in a three-neck flask, which was equipped with a thermometer, a condenser and a hydrotreater (including a hydrogen cylinder, hydrogen flowmeter, three-way valve and a nitrogen cylinder), with a magnetic stirrer. Under atmospheric pressure, 100 mL water solution of 4-CP (1%), 7.78 mmol NaOH and 20 mg 5% Pd/C were added into the flask. Alternatively, 100 mL water–ethanol (99:1, V:V) solution of 2,4-DCP (0.1%), 1.23 mmol NaOH and 20 mg 5% Pd/C were added into the flask. After the air in the flask was completely replaced by nitrogen gas, hydrogen gas was supplied at a constant flow of 10 mL min^{-1}. Then the reaction mixture was stirred with a magnetic stirrer and kept at 40 °C with a thermostated water bath.

Combination of HDC and biodegradation

As described above, the HDC of 4-CP and 2,4-DCP was carried out. After the reaction was stopped, the mixture was centrifuged (4,000 rpm for 10 min), and the concentration of CPs and phenol in supernatant solution were determined. Subsequently, aliquot supernatant solution was diluted into 30 mL by MSM and was inoculated by the yeast *C. tropicalis* (10^6 cells mL^{-1}). Nevertheless, the MSM herein do not contain NaCl. The biodegradation of phenol formed was also performed at 30 °C on a rotary shaker (200 rpm).

Analysis of chlorinated phenols

CPs and their intermediate products including phenol during HDC were determined by high performance liquid chromatography (HPLC) (Agilent 1200 Series LC, Agilent Technologies, USA), equipped with a Zorbax ODS C-18 column using mobile phase (methanol:water = 60:40) and a UV detector operating at 283 nm. The injection volume was 10 μL and the mobile phase flow rate was 1 mL min^{-1} at 25 °C. To measure phenol concentration of residual substrate, samples of suspended culture were centrifuged at 7,500 rpm for 10 min. The cell free supernatants were used to determine the substrate concentration by HPLC.

RESULTS AND DISCUSSION

Catalytic HDC of CPs

CPs had higher toxicity and stronger stability, and were more difficult to biodegrade than phenol due to the presence of chlorine (Figure 1). In particular, the more chlorine existing in the aromatic ring, the more non-biodegradability occurred. Figure 1 showed that after 9 days only about 11% of 2,4,6-TCP (100 mg L^{-1}) was degraded by *C. tropicalis*; whereas 300 mg L^{-1} of phenol was completely degraded within only 14 h. On the other hand, under the same experimental conditions, 2,4,6-TCP was catalytically oxidized after 9 h; whereas the oxidation of phenol was completed within only 13 min (Zhou *et al.* 2011). Therefore, it was difficult or impractical for abatement of CPs, especially polychlorinated phenols under mild conditions by biodegradation or catalytic wet peroxide oxidation, in view of the efficiency and cost.

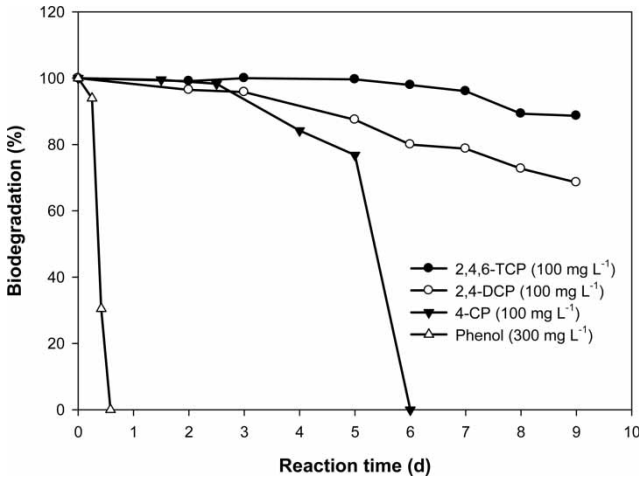

Figure 1 | The biodegradation of chlorinated phenols by *C. tropicalis*.

However, the catalytic HDC of CPs was easy to complete under mild conditions, as shown in Figure 2. During the HDC process of chlorinated organic compounds, HCl by-product formed, which might result in the deactivation of catalysts. So, some bases such as NaOH, equivalent to the amounts of chlorine were often used as scavengers of HCl to eliminate and minimize the poison to catalysts (Urbano & Marinas 2001; Yuan & Keane 2004). In addition, most of the organochlorine compounds including CPs are hydrophobic and thus have low solubility in water, which limits their HDC reaction. Usually, the catalytic HDC was performed in water–ethanol systems in order to take advantage of the better solubility of hydrogen in polar solvents (Wee & Cunningham 2008; Gómez-Quero *et al.* 2010).

Further, the HDC of 2,4-DCP was a stepwise process, yielding 2-chlorophenol (2-CP) as the only intermediate partially dechlorinated product, which was further converted to phenol (Figure 2). This was coincident with the results reported in the literature (Yuan & Keane 2004; Gómez-Quero *et al.* 2010). 2-CP was the only reactive intermediate product observed in terms of dechlorination, and the absence of 4-CP might be explained on the basis of steric hindrance of the hydroxyl group whereby the *ortho*-substituted Cl experienced a more restricted HDC (Yuan & Keane 2004; Gómez-Quero *et al.* 2010).

In a word, CPs with higher concentration could be dechlorinated within 60 min in either water or water–ethanol systems at ambient temperature and pressure. Moreover, the products were phenol and NaCl. Because phenol was easier to biodegrade or catalytically oxidize as mentioned above, the HDC reaction should be considered as one of best pre-treatment techniques.

Microbial degradation of phenol

A number of microorganisms that can grow on phenol as a sole carbon and energy source have been isolated, cultured, adapted and enriched in recent years (Agarry *et al.* 2008). Among which, a yeast *C. tropicalis* has been paid more attention for aerobically degrading phenol due to its rapid and high biodegradation ability, as well as its high resistance to salt (Bastos *et al.* 2000; Jiang *et al.* 2005; Varma & Gaikwad 2008; Wang *et al.* 2011). For example, Jiang *et al.* (2005) showed that *C. tropicalis* had high phenol degradation potential, which could thoroughly degrade the phenol of

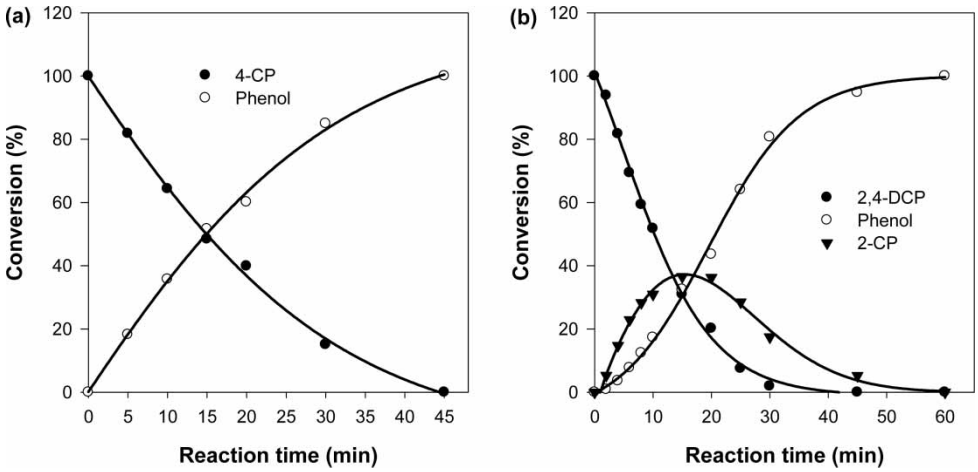

Figure 2 | Product distribution as a function of time during catalytic hydrodechlorination of (a) 4-CP and (b) 2,4-DCP over 5% Pd/C.

2 g L^{-1} within 66 h. Further, Varma & Gaikwad (2008) evidenced that the genus *Candida* could degrade 2 g L^{-1} phenol in 48 h, and *C. tropicalis* 3556 was the most efficient, as it rapidly degraded more than 95% of the compound in just 16 h. In addition, Bastos *et al.* (2000) proved that *C. tropicalis* tolerated higher concentration of salt (15%) than bacterium *Alcaligenes faecalis* (*A. faecalis*) (5.6%), which was another salt-tolerant phenol-degrading microorganism. At the same time, the yeast also tolerated a wider pH range (3–9) during phenol degradation than *A. faecalis* (pH 7–9).

C. tropicalis isolated from the sludge on the beach of the Yellow Sea also showed high ability to biodegrade phenol, which could degrade completely 900 mg L^{-1} phenol within 30 h (Figure 3). The phenol degradability data were fitted well with a Sigmoidal Gompertz equation (Figure 3 and Table 1):

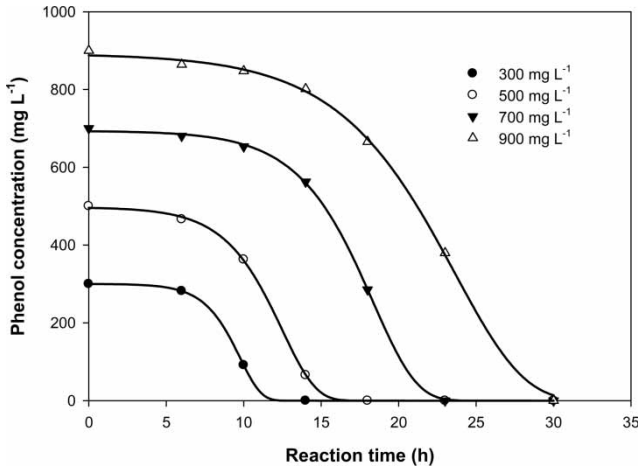

Figure 3 | Degradation kinetics of phenol by *C. tropicalis*.

$$Y = a\exp[-b\exp(-ct)] \quad (1)$$

where 'Y' is the substrate concentration at time 't' (mg L^{-1}); 'a' is the asymptotic value of the component (total potentially degradable fraction) (mg L^{-1}); 'b' is the relative degradation rate as affected by a constant factor of microbial efficiency ('c') and 't' is the time in hours (Bidlack & Buxton 1992).

Its first derivative and second derivative were as follows:

$$\frac{dY}{dt} = abc\ \exp[-b\exp(-ct)]\exp(-ct) \quad (2)$$

$$\frac{d^2Y}{dt^2} = ab^2c^2\,[\exp(-ct)]^2\exp[-b\exp(-ct)] - abc^2\exp[-b\exp(-ct)]\exp(-ct) \quad (3)$$

The times of maximum degradation rate (t_{μ_m}) were determined by setting the second derivative of the Gompertz function equal to zero and solving for 't', accordingly, the maximum degradation rates (μ_m) were determined by calculating the first derivative with respect to t_{μ_m}. In addition, the lag phase time (λ) was also determined based on the minimum value of the second derivative of the Gompertz function.

Table 1 showed that λ as well as t_{μ_m} was prolonged with increasing phenol concentration due to the endurance of *C. tropicalis* to phenol; however, the maximum value of μ_m occurred for middle concentration of phenol, i.e. 700 mg L^{-1}. Usually, there was a decrease in biodegradation rate as initial phenol concentration increased, due to

Table 1 | Phenol degradability kinetic parameters estimated with Gompertz model

Phenol concentration (mg L^{-1})	a (mg L^{-1})	b	c	t_{μ_m} (h)	μ_m (mg L^{-1} h^{-1})	λ (h)	R^2	p
300	300.23	7.78×10^{-4}	−0.73	9.76	80.98	8.45	1	<0.0001
500	497.36	3.31×10^{-3}	−0.46	12.48	83.73	10.37	0.9998	<0.0001
700	693.73	1.50×10^{-3}	−0.35	18.34	90.48	15.61	0.9998	<0.0001
900	892.13	4.95×10^{-3}	−0.22	23.63	73.73	19.34	0.9993	<0.0001

the inhibitory effect of phenol. It was unclear why the maximum degradation rate increased with the increase of phenol concentration from 300 mg L^{-1} up to 700 mg L^{-1}, then decreased markedly. Banerjee & Ghoshal (2010) also found that in the phenol concentration range of 100–2,000 mg L^{-1}, the maximum degradation rate was obtained at an initial phenol concentration of about 800 mg L^{-1} for the strain AKG1 and about 200 mg L^{-1} for the strain AKG2. However, they did not give a reasonable explanation. El-Naas *et al.* (2009) considered that the lower biodegradation rate at low phenol concentrations was due to mass transfer control, whereby less phenol was accessible for the biomass; whereas an increase in the initial phenol concentration beyond a certain value reduced the removal rate of phenol, which could be attributed to the inhibitory effect of phenol. However in their experiments, phenol was biodegraded by *Pseudomonas putida*, immobilized in polyvinyl alcohol gel. In most of the reaction systems where microbes grew in MSM, maybe the mass transfer was not the dominant factor. In a word, it is difficult to explain the change mechanism of μ_m with phenol concentration. Probably, there were complicated interactions among the interface transfer of microbe and phenol, the growth of microbes and the inhibitory effect of phenol.

Obviously, it is feasible to combine HDC with biodegradation for rapid abatement of recalcitrant organochlorine pollutants. Nevertheless, the catalytic HDC was usually performed in water–ethanol systems in order to promote dechlorination efficiency (Wee & Cunningham 2008; Gómez-Quero *et al.* 2010). Therefore, it is necessary to focus more attention on the effect of ethanol on biodegradation of phenol when the combination method of HDC and biodegradation was used to destroy polychlorinated phenols.

Effect of ethanol dosage on the biodegradation of phenol

On the one hand, ethanol as a carbon source could stimulate the growth of *C. tropicalis*. On the other hand, ethanol might inhibit the expression of catabolic genes (coding for phenol hydroxylase and catechol 1,2-dioxygenase) (Lovanh & Alvarez 2004; Agarry *et al.* 2008). Thus, ethanol would play a double role in biodegradation of phenol, that is, it is advantageous, as well as going against the biodegradation of phenol, which is probably dependent on its dosage. Figure 4 and Table 2 showed that λ and t_{μ_m} increased with the increase in ethanol dosage, which led to complete inhibition of phenol biodegradation or cell death of *C. tropicalis* when ethanol dosage increased to 0.8%. However, ethanol dosage less than a certain value such as 0.48% caused a great increase in μ_m (Table 2),

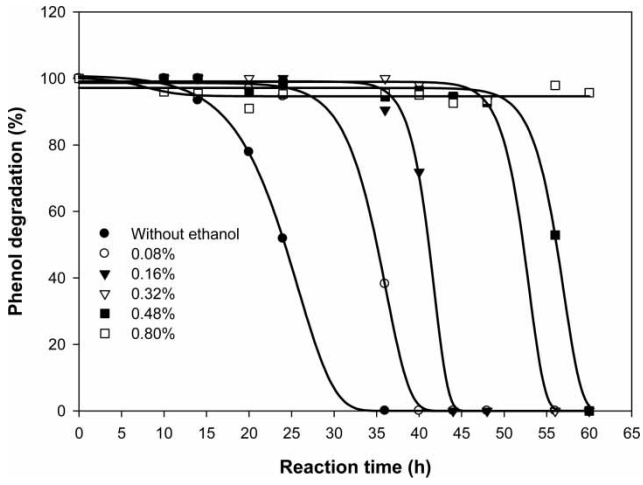

Figure 4 | Effect of ethanol dosage on degradation of phenol by *C. tropicalis*.

Table 2 | Effect of ethanol dosage on phenol degradability kinetic parameters

Ethanol dosage (%)	t_{μ_m} (h)	μ_m (mg L^{-1} h^{-1})	λ (h)
0	25.74	69.12	21.61
0.08	36.11	104.36	33.43
0.16	41.77	177.30	40.19
0.32	52.95	157.65	51.17
0.48	57.01	136.73	55.0
0.80	–	–	–

suggesting that although it caused the modest increase in the duration of the lag phase, a certain mass of ethanol promoted phenol biodegradability by supplying *C. tropicalis* with an adequate carbon source. Herein, we considered that it was acceptable for ethanol dosage up to 0.5%. Of course, about 0.16% ethanol was the best for biodegradation of phenol by *C. tropicalis* due to its lower λ and having the highest μ_m.

Combination of HDC and biodegradation for abatement of CPs

Candida tropicalis has high biodegradability to phenol and high resistance to salt (Bastos *et al*. 2000; Jiang *et al*. 2005; Varma & Gaikwad 2008; Wang *et al*. 2011); at the same time, it has a stronger tolerance to ethanol. Therefore, the moderately diluted suspension after the catalytic HDC of CPs, containing phenol and NaCl with or without ethanol, should be rapidly biodegraded by *C. tropicalis*.

In our experiments, for the HDC in water systems, the centrifugal solution was diluted to the degree whereby the concentration of phenol was less than 1,000 mg L^{-1}; for the HDC in water–ethanol systems, the diluted solution was made so that the content of ethanol was not more than 0.5%. Based on these preconditions, after the HDC of 4-CP and 2,4-DCP was stopped, the centrifugal solution was diluted 10 times and two times with MSM, respectively.

Table 3 shows the biodegradation of phenol from the centrifugal solution of the HDC reaction. After catalytic HDC to discover whether 4-CP or 2,4-DCP was completed, the reaction solution could be subsequently biodegraded by *C. tropicalis*. This means that the combination method of HDC and biodegradation for rapid abatement of recalcitrant organochlorine pollutants with higher concentration under mild conditions was tried and true.

Table 3 | The biodegradation of phenol by *C. tropicalis* after the HDC of 4-CP and 2,4-DCP

Sample	Phenol concentration (mg L^{-1})	Sample	Phenol concentration (mg L^{-1})
After HDC of 4-CP	731.8	After HDC of 2,4-DCP	288.5
Biodegradation, in hours		Biodegradation, in hours	
8	712.6	8	288.2
12	693.2	12	284.0
16	538.0	16	279.8
20	210.2	20	280.1
24	0	24	273.6
		32	266.8
		36	148.0
		40	0

A simple, safe, and efficient technology for the abatement of recalcitrant pollutants in wastewater is critical to water recycle and environmental safety. Our study revealed that CPs with higher concentration could be completely dechlorinated at ambient temperature and pressure, and the HDC suspension was subsequently biodegraded by a yeast *C. tropicalis*. That is, compared with the conventional abatement methods, our strategy based on the combined use of HDC and biodegradation is efficient, time saving, and inexpensive; further, it could be applied in a simple and mild way, and secondary pollution could be avoided. Thus, combination of HDC and biodegradation for abatement of recalcitrant organochlorine compounds with higher concentration in wastewater is promising, and more attention should be paid to this field.

CONCLUSIONS

The combination method of catalytic HDC over Pd/C and biodegradation by *C. tropicalis* for abatement of 4-CP and 2,4-DCP was studied. The results revealed that 4-CP and 2,4-DCP could be easily and completely dechlorinated under mild conditions, ultimately yielding phenol as product. Phenol (0–900 mg L^{-1}) could be completely degraded by *C. tropicalis* within 30 h, and the degradability data were fitted well with a Sigmoidal Gompertz equation. Moreover, during the biodegradation of phenol, ethanol played a double role, whereby definite mass of ethanol caused a modest increase in the duration of the lag phase, but led to a great increase in the maximum degradation rates. Ethanol dosage up to 0.5% was acceptable for the biodegradation of phenol. Our experiments evidenced that after the HDC of 4-CP and 2,4-DCP was completed, the suspension containing phenol and NaCl with and without ethanol, could be rapidly biodegraded by *C. tropicalis*. This means that CPs with higher concentration could be efficiently detoxified under mild conditions by combination of HDC and biodegradation in water or water–ethanol systems. That is, the combination method of HDC and biodegradation for rapid abatement of recalcitrant organochlorine pollutants with higher concentration under mild conditions was promising, and was tried and true.

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